Chapter 20

THE HALOGENS:
FLUORINE, CHLORINE,
BROMINE, IODINE,
AND ASTATINE

20-1 Introduction

With the exception of He, Ne, and Ar, all of the elements in the periodic table form halides. Ionic or covalent halides are among the most important and common compounds. They are often the easiest to prepare and are widely used as source materials for the synthesis of other compounds. Where an element has more than one valence, the halides are often the best known and most accessible compounds in all of the oxidation states. There is also an extensive and varied chemistry of organic halogen compounds; the fluorine compounds, especially where F completely replaces H, have unique properties.

The position of the elements in the periodic table is outlined in Section 2-5, and some properties are listed in Table 8-7. The element astatine, named for the Greek for "unstable," has no stable isotope. As far as can be ascertained by tracer studies, At behaves like I, but is perhaps somewhat less electronegative.

20-2 Occurrence, Isolation, and Properties of the Elements

Fluorine occurs widely, for example as CaF₂ (fluorspar), Na₃AlF₆ (cryolite), and 3Ca₃(PO₄)₂Ca(F,Cl)₂ (fluorapatite). It is more abundant than chlorine. Fluorine was first isolated in 1886 by H. Moissan. The element is obtained by electrolysis of molten fluorides. The most commonly used electrolyte is KF·2-3HF (mp 70–100 °C). As the electrolysis proceeds the melting point increases, but the electrolyte is readily regenerated by resaturation with HF from a storage tank. Fluorine cells are constructed of steel, Cu, or Ni–Cu alloy, which become coated with an unreactive layer of fluoride. The cathodes are steel or Cu, the anodes ungraphitized carbon. Although F₂ is often handled in metal apparatus, it can be handled in glass provided traces of HF, which attacks glass rapidly, are removed by passing the gas through anhydrous NaF or KF with which HF forms the bifluorides (MHF₂).

Fluorine is the most chemically reactive of all the elements and combines directly (often with extreme vigor), at ordinary or elevated temperatures, with all the elements other than O₂, He, Ne, and Kr. It also attacks many other com-
pounds, breaking them down to fluorides; organic materials often inflame and burn in F₂.

The great reactivity of F₂ is in part attributable to the low dissociation energy (Table 1-1) of the F—F bond, and because reactions of atomic fluorine are strongly exothermic. The low F—F bond energy is probably due to repulsion between nonbonding electrons. A similar effect may account for the low bond energies in H₂O₂ and N₂H₄.

Chlorine occurs as NaCl, KCl, MgCl₂, and so on, in seawater, salt lakes, and as deposits originating from the prehistoric evaporation of salt lakes. Chlorine is obtained by electrolysis of brine. Older technology employed a mercury cathode in which the sodium dissolved.

\[
\text{Na}^+ + e^- = \text{Na} \quad (20-2.1)
\]
\[
\text{Cl}^- = \frac{1}{2} \text{Cl}_2 + e^- \quad (20-2.2)
\]

However, this process entailed a hazard because of the loss of mercury to the environment, and a newer process employing membrane cells and not requiring mercury is now common.

Chlorine is a greenish gas. It is moderately soluble in water, with which it reacts as in Reaction 20-2.3.

\[
\text{Cl}_2 + \text{H}_2\text{O} = \text{HCl} + \text{HOCl} \quad (20-2.3)
\]

Bromine occurs in much smaller amounts, as bromides, along with chlorides. Bromine is obtained from brines by the reaction:

\[
2 \text{Br}^- + \text{Cl}_2 \xrightarrow{\text{pH ~}3.5} 2 \text{Cl}^- + \text{Br}_2 \quad (20-2.4)
\]

It is swept out in a current of air. Bromine is a dense, mobile, dark red liquid at room temperature. It is moderately soluble in water and miscible with nonpolar solvents such as CS₂ and CCl₄.

Iodine occurs as iodide in brines and as iodate in Chile saltpeter (guano, NaNO₃). Various forms of marine life concentrate iodine. Production of I₂ involves either oxidizing I⁻ or reducing iodates to I⁻ followed by oxidation. An acid solution of MnO₂ is commonly used as the oxidant.

Iodine is a black solid with a slight metallic luster. At atmospheric pressure it sublimes without melting. It is readily soluble in nonpolar solvents such as CS₂ and CCl₄. Such solutions are purple, as is the vapor. In polar solvents, unsaturated hydrocarbons, and liquid SO₂, brown or pinkish-brown solutions are formed. These colors indicate the formation of weak complexes I₂⁻·S known as charge-transfer complexes. The bonding energy results from partial transfer of charge in the sense I₂⁻·S. The complexes of I₂ and also of Br₂, Cl₂, and ICl can sometimes be isolated as crystalline solids at low temperatures.

Iodine forms a blue complex with starch, in which the iodine forms linear I₅⁻ ions in channels in the polysaccharide amylose.

Astatine has been identified as a short-lived product in the natural radioactive decay series of uranium and thorium. The element was first obtained in quantities sufficient for study by the \(^{209}\text{Bi}(\alpha,2n)^{211}\text{At}\) reaction (Chapter 1). About 20 isotopes of astatine are known, but the longest lived has a half-life of only 8.3 h. As a result, macroscopic quantities cannot normally be isolated for
synthetic purposes, although a few inorganic compounds (HAt, CH₃At, AtI, AtBr, and AtCl) have been detected by mass spectrometry. Astatine appears to behave chemically about as would be expected on extrapolation of the properties of the other halogens. It is rather volatile and somewhat soluble in water. A few organic compounds, such as C₆H₅At, C₆H₅AtCl₂, and C₆H₅AtO₂ are known.

20-3 Halides

There are almost as many ways of classifying halides as there are types of halides. Binary halides may form simple molecules, or complex, infinite arrays. For ionic compounds some common types of lattices are given in Chapter 4 and some general points on halides are discussed in Section 5-5. Other types of halide compounds include oxide halides such as VOCl₃, hydroxy halides, and organohalides. The covalent and ionic radii are given in Table 8-7.

Preparation of Anhydrous Halides

1. Direct interaction with the elements. The halogens themselves are normally used for most elements. The compounds HF, HCl, and HBr may also be used for metals.

Direct fluorination normally gives fluorides in the higher oxidation states. Most metals and nonmetals react very vigorously with F₂; with nonmetals such as P₄, the reaction may be explosive. For rapid formation in dry reactions of chlorides, bromides, and iodides elevated temperatures are usually necessary. For metals, the reaction with Cl₂ and Br₂ may be more rapid when THF or some other ether is used as a reaction medium; the halide is then obtained as a solvate.

2. Dehydration of hydrated halides. The dissolution of metals, oxides, or carbonates in aqueous halogen acids followed by evaporation or crystallization gives hydrated halides. These can sometimes be dehydrated by heating in vacuum, but this often leads to impure products or oxohalides. Dehydration of chlorides can be effected by thionyl chloride, and halides in general can be treated with 2,2-dimethoxypropane.

\[
\text{CrCl₃} \cdot 6 \text{H₂O} + 6 \text{SOCl₂} \xrightarrow{\text{reflux}} \text{CrCl₃} + 12 \text{HCl} + 6 \text{SO₂}
\]  (20-3.1)

MXₙ \cdot m \text{H₂O in CH₃C(OCH₃)₂CH₃} \xrightarrow{} MXₙ + m(\text{CH₃})₂\text{CO} + 2m \text{CH₃OH}
\]  (20-3.2)

The acetone and methanol products of Reaction 20-3.2 may solvate the halide products, but the solvents can easily be removed by gentle heating or at reduced pressures.

3. Treatment of oxides with other halogen compounds. Oxides may often be treated with halogen-containing compounds to replace oxygen with halogen, as in the following reactions:

\[
\text{NiO} + 3 \text{ClF}_₃ \xrightarrow{} \text{NiF}_₂ + \cdots
\]  (20-3.3)

\[
\text{Pr}_₂\text{O}_₃ + 6 \text{NH₄Cl} \xrightarrow{300^\circ \text{C}} 3 \text{PrCl}_₃ + 3 \text{H₂O} + 6 \text{NH₃}
\]  (20-3.4)

\[
\text{Sc}_₂\text{O}_₃ + 4 \text{CCl}_₄ \xrightarrow{600^\circ \text{C}} \text{ScCl}_₄ + \cdots
\]  (20-3.5)

4. Halogen exchange. Many halides react to exchange halogen with (a) elemental halogens, (b) acid halides, (c) halide salts, or (d) an excess of another
halogen-containing substance. Chlorides can often be converted to either bromides (by KBr) or especially to iodides (by KI), using acetone, in which KCl is less soluble. Halogen exchange is especially important for the synthesis of fluorides from chlorides, using various metal fluorides such as CoF₃ or AsF₅. This type of replacement is used extensively in the synthesis of organic fluorine compounds, as discussed in Section 20-7.

Another fluorinating agent that has special advantages is SbF₅, which is used along with SbCl₅ as a catalyst in Reaction 20-3.6.

\[
C₆H₅CCl₃ + SbF₅ \rightarrow C₆H₅CF₃ + SbCl₅ \quad (20-3.6)
\]

**Molecular Halides**

Most of the electronegative elements, and the metals in high oxidation states, form molecular halides. These halides are gases, liquids, or volatile solids with molecules held together only by van der Waals forces. There is probably a rough correlation between increasing metal-to-halogen covalence and increasing tendency to the formation of molecular compounds. Thus the molecular halides are sometimes also called the covalent halides. The designation molecular is preferable, since it states a fact.

The formation of halide bridges between two or, less often, three other atoms is an important structural feature. Between two metal atoms, the most common situation involves two halogen atoms, but examples with one and three bridge atoms are known. Such bridges used to be depicted as involving a covalent bond to one metal atom and donation of an electron pair to the other as in Structure 20-1, but structural data show that the two bonds to each bridging halogen atom are usually equivalent as in Structure 20-II. Molecular orbital theory provides a simple, flexible formulation in which the M-X-M group is treated as a three-center, four-electron (3c-4e) group (cf. Section 3-7).

With Cl⁻ and Br⁻, bridges are characteristically bent, whereas fluoride bridges may be either bent or linear. Thus, in BeF₂ there are infinite chains, \(-\cdots BeF₂BeF₂\cdots\), with bent bridges, similar to the situation in BeCl₂. On the other hand, transition metal pentahalides afford a notable contrast. While the pentachlorides dimerize with bent M-Cl-M bridges (Structure 20-II), the pentafluorides form cyclic tetramers with linear M-F-M bridges (Structure 20-III). The fluorides probably adopt the tetrameric structures with linear bridges, in part because the smaller size of F than of Cl would introduce excessive metal-metal repulsion in a bent bridge.

**Molecular fluorides** of both metals and nonmetals are usually gases or volatile liquids. Their volatility is due to the absence of intermolecular bonding other
than van der Waals forces, since the polarizability of fluorine is very low and no suitable outer orbitals exist for other types of attraction. Where the central atom has suitable vacant orbitals available, and especially if the polarity of the single bonds M—F would be such as to leave a considerable charge on M, as in, say, SF₆, multiple bonding can occur using filled p orbitals of fluorine for overlap with vacant orbitals of the central atom. This multiple bonding is a major factor in the shortness and high strength of many bonds to fluorine. Because of the high electronegativity of fluorine the bonds in these compounds tend to be very polar. Because of the low dissociation energy of F₂ and the relatively high energy of many bonds to F (e.g., C—F, 486; N—F, 272; P—F, 490 kJ mol⁻¹), molecular fluorides are often formed very exothermically.

The high electronegativity of fluorine often has a profound effect on the properties of molecules in which several F atoms occur. Representative examples include (a) CF₃CO₂H is a strong acid; (b) (CF₃)₃N and NF₃ have no basicity; and (c) CF₃ derivatives in general are attacked much less readily by electrophilic reagents in anionic substitutions than are CH₃ compounds. The CF₃ group may be considered as a kind of large pseudohalogen with an electronegativity about comparable to that of Cl.

A fairly general property of molecular halides is their easy hydrolysis, for example,

\[
\begin{align*}
\text{BCl}_3 + 3 \text{H}_2\text{O} & \longrightarrow \text{B(OH)}_3 + 3 \text{H}^+ + 3 \text{Cl}^- \quad \text{(20-3.7)} \\
\text{PBr}_3 + 3 \text{H}_2\text{O} & \longrightarrow \text{HPO(OH)}_2 + 3 \text{H}^+ + 3 \text{Br}^- \quad \text{(20-3.8)} \\
\text{SiCl}_4 + 4 \text{H}_2\text{O} & \longrightarrow \text{Si(OH)}_4 + 4 \text{H}^+ + 4 \text{Cl}^- \quad \text{(20-3.9)}
\end{align*}
\]

Where the maximum covalency is attained, as in CCl₄ or SF₆, the halides may be quite inert towards water. However, this is a result of kinetic and not thermodynamic factors. For instance, for CF₄, the equilibrium for hydrolysis, as in Reaction 20-3.10

\[
\text{CF}_4(\text{g}) + 2 \text{H}_2\text{O}(\ell) = \text{CO}_2(\text{g}) + 4 \text{HF}(\text{g}) \quad \text{(20-3.10)}
\]

is thermodynamically favorable \((K_{eq} = 10^{23})\), but the rate of hydrolysis is negligible because there is no site for attack by water at carbon. The necessity for means of attack is also illustrated by the fact that SF₆ is not hydrolyzed, whereas SeF₆ and TeF₆ are hydrolyzed at 25 °C. Attack by a nucleophile (and expansion of the coordination sphere) is possible only for Se and Te, not S.

### 20-4 Halogen Oxides

Oxygen fluorides have been studied as potential rocket fuel oxidizers. Oxygen difluoride (OF₂) is obtained as a pale yellow gas on passing F₂ gas rapidly through a 2% NaOH solution. Dioxygen difluoride (O₃F₂) is an unstable orange-yellow solid made by the action of electric discharges on F₂—O₂ mixtures; O₃F₂ is an extremely potent oxidizing and fluorinating agent.

Chlorine oxides are reactive, and tend to explode. None can be obtained by direct reaction of Cl₂ and O₂. The dioxide (ClO₂) is a powerful oxidant and is used diluted with air commercially, for example, for bleaching wood pulp. It is always
made “on site” by Reaction 20-4.1

\[
2 \text{NaClO}_3 + \text{SO}_2 + \text{H}_2\text{SO}_4 = 2 \text{ClO}_2 + 2 \text{NaHSO}_4
\] (20-4.1)

or by reduction of KClO\(_3\) with moist oxalic acid at 90 °C, carbon dioxide being an additional product. Chlorine dioxide is monomeric (Structure 20-IV), but in the crystal the molecules associate loosely, pairwise as in Structure 20-V, and the solid becomes diamagnetic at low temperatures.

\[
\begin{align*}
\text{ClO}_2 & \quad \text{Structure 20-IV} \\
\text{ClO}_2 & \quad \text{Structure 20-V}
\end{align*}
\]

The compound Cl\(_2\)O is used as a selective and powerful chlorinating agent for organic compounds. It can also be passed into lime water to make Ca(OCl\(_2\)), a safe and useful bleaching agent.

**Iodine pentoxide** is the anhydride of iodic acid, and can be prepared by dehyd­dration of iodic acid at elevated temperatures, as in Reaction 20-4.2.

\[
2 \text{HIO}_3 \xrightleftharpoons[240 ^\circ\text{C}]{\text{H}_2\text{O}} \text{I}_2\text{O}_5 + \text{H}_2\text{O}
\] (20-4.2)

Iodine pentoxide is an oxidizing agent that can be used in the determination of CO, as in Reaction 20-4.3

\[
5 \text{CO} + \text{I}_2\text{O}_5 = \text{I}_2 + 5 \text{CO}_2
\] (20-4.3)

where the liberated iodine is determined by iodometry. Iodine pentoxide has a three-dimensional network structure with O\(_2\)I—O—I\(_2\)O units linked by strong intermolecular I⋯O interactions.

### 20-5 The Oxo Acids

The chemistry of the halogen oxo acids is complicated. Solutions of the acids and several of the anions may be obtained by interaction of the free halogens with water or aqueous bases. In this section the term halogen refers to Cl, Br, and I only; fluorine forms only FOH as discussed in the following subsection.

#### Reaction of Halogens with H\(_2\)O and OH\(^-\)

The potentials and equilibrium constants necessary to understand these systems can be derived from data given in Table 20-1.

The halogens are all soluble in water to some extent. However, in such solutions there are species other than solvated halogen molecules, since a disproportionation reaction occurs rapidly.

\[
\begin{align*}
\text{X}_2(\text{g,} \ell, \text{s}) & = \text{X}_2(\text{aq}) & K_1 \\
\text{X}_2(\text{aq}) & = \text{H}^+ + \text{X}^- + \text{HOX} & K_2
\end{align*}
\] (20-5.1) (20-5.2)
Table 20-1  Standard Potentials (in V) for Reactions of Halogen Compounds

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)  $\text{H}^+ + \text{HOX} + e^- = \frac{1}{2} \text{X}_2(g,\ell,s) + \text{H}_2\text{O}$</td>
<td>1.63</td>
<td>1.59</td>
<td>1.45</td>
</tr>
<tr>
<td>(2)  $3 \text{H}^+ + \text{HXO}_2 + 3 e^- = \frac{3}{2} \text{X}_2(g,\ell,s) + 2 \text{H}_2\text{O}$</td>
<td>1.64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3)  $6 \text{H}^+ + \text{XO}_5^- + 5 e^- = \frac{5}{2} \text{X}_2(g,\ell,s) + 3 \text{H}_2\text{O}$</td>
<td>1.47</td>
<td>1.52</td>
<td>1.20</td>
</tr>
<tr>
<td>(4)  $8 \text{H}^+ + \text{XO}_4^- + 7 e^- = \frac{7}{2} \text{X}_2(g,\ell,s) + 4 \text{H}_2\text{O}$</td>
<td>1.42</td>
<td>1.59</td>
<td>1.34</td>
</tr>
<tr>
<td>(5)  $\frac{1}{2} \text{X}_2(g,\ell,s) + e^- = \text{X}^-$</td>
<td>1.36</td>
<td>1.07</td>
<td>0.54*</td>
</tr>
<tr>
<td>(6)  $\text{XO}^- + \text{H}_2\text{O} + 2 e^- = \text{X}^- + 2 \text{OH}^-$</td>
<td>0.89</td>
<td>0.76</td>
<td>0.49</td>
</tr>
<tr>
<td>(7)  $\text{XO}_2 + 2 \text{H}_2\text{O} + 4 e^- = \text{X}^- + 4 \text{OH}^-$</td>
<td>0.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(8)  $\text{XO}_3^- + 3 \text{H}_2\text{O} + 6 e^- = \text{X}^- + 6 \text{OH}^-$</td>
<td>0.63</td>
<td>0.61</td>
<td>0.26</td>
</tr>
<tr>
<td>(9)  $\text{XO}_4^- + 4 \text{H}_2\text{O} + 8 e^- = \text{X}^- + 8 \text{OH}^-$</td>
<td>0.56</td>
<td>0.69</td>
<td>0.39</td>
</tr>
</tbody>
</table>

*Indicates that I$^-$ can be oxidized by oxygen in aqueous solution.

The values of $K_1$ are Cl$^2$, 0.062; Br$^2$, 0.21; I$^2$, 0.0013. The values of $K_2$ computed from the potentials in Table 20-1 are $4.2 \times 10^{-4}$ for Cl$^2$, $7.2 \times 10^{-9}$ for Br$^2$, and $2.0 \times 10^{-13}$ for I$^2$. We can also estimate from

$$\frac{1}{2} \text{X}_2 + e^- = \text{X}^- \quad (20-5.3)$$

and

$$\text{O}_2 + 4 \text{H}^+ + 4 e^- = 2 \text{H}_2\text{O} \quad E^\circ = 1.23 \text{ V} \quad (20-5.4)$$

that the potentials for the reactions

$$2 \text{H}^+ + 2 \text{X}^- + \frac{1}{2} \text{O}_2 = \text{X}_2 + \text{H}_2\text{O} \quad (20-5.5)$$

are −1.62 V for fluorine, −0.13 V for chlorine, 0.16 V for bromine, and 0.69 V for iodine.

Thus for saturated solutions of the halogens in water at 25 °C we have the results shown in Table 20-2. There is an appreciable concentration of HOCl in a saturated aqueous solution of Cl$^2$, a smaller concentration of HOBr in a saturated solution of Br$^2$, but only a negligible concentration of HOI in a saturated solution of I$^2$.

Hypohalous Acids

The colorless, very unstable gas FOH is made by passing F$^2$ over ice and collecting the gas in a trap. It reacts rapidly with water. The other XOH compounds are

Table 20-2  Equilibrium Concentrations in Aqueous Solutions of the Halogens (25 °C, mol L$^{-1}$)

<table>
<thead>
<tr>
<th></th>
<th>Cl$^2$</th>
<th>Br$^2$</th>
<th>I$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solubility</td>
<td>0.091</td>
<td>0.21</td>
<td>0.0013</td>
</tr>
<tr>
<td>Concentration $\text{X}_2(\text{aq})$, (mol L$^{-1}$)</td>
<td>0.061</td>
<td>0.21</td>
<td>0.0013</td>
</tr>
<tr>
<td>$[\text{H}^+] = [\text{X}^-] = [\text{HOX}]$</td>
<td>0.030</td>
<td>$1.15 \times 10^{-3}$</td>
<td>$6.4 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
also unstable. They are known only in solution from the interaction of the halogen and Hg\textsuperscript{II} oxide.

\[ 2 \text{X}_2 + 2 \text{HgO} + \text{H}_2\text{O} \rightarrow \text{HgO} \cdot \text{HgX}_2 + 2 \text{HOX} \]  

(20-5.6)

The hypohalous acids are very weak acids but good oxidizing agents, especially in acid solution (see Table 20-1).

The hypohalite ions can be produced in principle by dissolving the halogens in base according to the general reaction

\[ \text{X}_2 + 2 \text{OH}^- \rightarrow \text{XO}^- + \text{X}^- + \text{H}_2\text{O} \]  

(20-5.7)

and for these rapid reactions the equilibrium constants are all favorable: $7.5 \times 10^{15}$ for Cl\textsubscript{2}, $2 \times 10^8$ for Br\textsubscript{2}, and 30 for I\textsubscript{2}.

However, the hypohalite ions tend to disproportionate in basic solution to produce the halate ions.

\[ 3 \text{XO}^- = 2 \text{X}^- + \text{XO}_3^- \]  

(20-5.8)

For these reactions, the equilibrium constants are very favorable: $10^{27}$ for ClO\textsuperscript{-}, $10^{15}$ for BrO\textsuperscript{-}, and $10^{20}$ for IO\textsuperscript{-}. Thus the actual products obtained on dissolving the halogens in base depend on the rates at which the hypohalite ions that were initially produced undergo disproportionation. These rates vary with temperature.

The disproportionation of ClO\textsuperscript{-} is slow at and below room temperature. Thus, when Cl\textsubscript{2} reacts with base “in the cold,” reasonably pure solutions of Cl\textsuperscript{-} and ClO\textsuperscript{-} are obtained. In hot solutions (~75 °C) the rate of disproportionation is fairly rapid and good yields of ClO\textsubscript{3}\textsuperscript{-} can be secured.

The disproportionation of BrO\textsuperscript{-} is moderately fast even at room temperature. Solutions of BrO\textsuperscript{-} can only be made and/or kept at around 0 °C. At temperatures of 50–80 °C quantitative yields of BrO\textsubscript{3} are obtained.

\[ 3 \text{Br}_2 + 6 \text{OH}^- \rightarrow 5 \text{Br}^- + \text{BrO}_3^- + 3 \text{H}_2\text{O} \]  

(20-5.9)

The rate of disproportionation of IO\textsuperscript{-} is so fast that it is unknown in solution. Hence, reaction of I\textsubscript{2} with base gives IO\textsubscript{3}\textsuperscript{-} quantitatively according to an equation analogous to that for Br\textsubscript{2}.

**Halous Acids**

The only certain acid is chlorous acid (HClO\textsubscript{2}). This acid is obtained in aqueous solution by treating a suspension of barium chlorite with H\textsubscript{2}SO\textsubscript{4}, and filtering off the BaSO\textsubscript{4}. It is a relatively weak acid ($K_a = 10^{-2}$) and cannot be isolated. Chlorites (MC\textsubscript{2}O\textsubscript{5}) are obtained by reaction of ClO\textsubscript{2} with solutions of bases.

\[ 2 \text{ClO}_2 + 2 \text{OH}^- \rightarrow \text{ClO}_2^- + \text{ClO}_3^- + \text{H}_2\text{O} \]  

(20-5.10)

Chlorites are used as bleaching agents. In alkaline solution ClO\textsubscript{2} is quite stable even on boiling. In acid solutions, the decomposition is rapid and is catalyzed by Cl\textsuperscript{-}.
Iodic acid, $\text{HIO}_3$, is a stable white solid obtained by oxidizing $\text{I}_2$ with concentrated $\text{HNO}_3$, $\text{H}_2\text{O}_2$, $\text{O}_3$, and so on. Chloric and bromic acids are obtained in solution by treating the barium halates with $\text{H}_2\text{SO}_4$.

The halic acids are strong acids and are powerful oxidizing agents. The ions $\text{XO}_3$ are pyramidal, as is to be expected from the presence of an octet, with one unshared pair in the halogen valence shell, that is, an $\text{AB}_3\text{E}$ species.

Iodates of the +4 ions of Ce, Zr, Hf, and Th can be precipitated from 6 $M$ nitric acid to provide a useful means of separation.

**Halates and Perhalates**

Although disproportionation of $\text{ClO}_3$ is thermodynamically very favorable,

$$4 \text{ClO}_3^- = \text{Cl}^- + 3 \text{ClO}_4^- \quad K = 10^{-29} \quad (20-5.12)$$

the reaction occurs very slowly in solution and is not a useful preparative procedure. Perchlorates are prepared by electrolytic oxidation of chlorates. The properties of perchloric acid are discussed in Section 7-11 and perchlorates are discussed in Section 5-3.

The disproportionation of $\text{BrO}_3$ to $\text{BrO}_4$ and $\text{Br}^-$ is extremely unfavorable ($K < 10^{-33}$). Perbromates can be obtained only by oxidation of $\text{BrO}_5^-$, preferably by $\text{F}_2$, in basic solution.

$$\text{BrO}_5^- + \text{F}_2 + 2 \text{OH}^- = \text{BrO}_4^- + 2 \text{F}^- + \text{H}_2\text{O} \quad (20-5.13)$$

The perbromates are exceedingly powerful oxidants.

$$\text{BrO}_4^- + 2 \text{H}^+ + 2 \text{e}^- = \text{BrO}_5^- + \text{H}_2\text{O} \quad E^\circ = +1.76 \text{ V} \quad (20-5.14)$$

Solutions of $\text{HBrO}_4$ up to 6 $M$ are stable, but decompose when stronger. Periodates resemble tellurates in their stoichiometries. The main equilibria in acid solutions are

$$\text{H}_5\text{IO}_6 = \text{H}^+ + \text{H}_4\text{IO}_6^- \quad K = 1 \times 10^{-3} \quad (20-5.15)$$

$$\text{H}_4\text{IO}_6^- = \text{IO}_4^- + 2 \text{H}_2\text{O} \quad K = 29 \quad (20-5.16)$$

$$\text{H}_4\text{IO}_6^- = \text{H}^+ + \text{H}_3\text{IO}_6^{2-} \quad K = 2 \times 10^{-7} \quad (20-5.17)$$

In aqueous solutions at 25 °C the main ion is $\text{IO}_4^-$. The pH-dependent equilibria are established rapidly. Kinetic studies of the hydration of $\text{IO}_4^-$ suggest either one-step or two-step paths (Fig. 20-1), the latter being more likely. Periodic acid and its salts are used in organic chemistry as oxidants that usually react smoothly and rapidly. They are useful analytical oxidants; for example, they oxidize $\text{Mn}^{2+}$ to $\text{MnO}_4^-$. 

$$5 \text{HClO}_2 \rightarrow 4 \text{ClO}_2 + \text{Cl}^- + \text{H}^+ + 2 \text{H}_2\text{O} \quad (20-5.11)$$
20-6 Interhalogen Compounds

The halogens form many compounds among themselves in binary combinations that may be neutral or ionic (e.g., BrCl, IF₅, Br₃⁺, I₅⁻). Ternary combinations occur only in polyhalide ions (e.g., IBrCl⁻).

Neutral interhalogen compounds are of the type XXₙ⁺, where n is an odd number, and X' is always the lighter halogen when n > 1. Because n is odd, the compounds are diamagnetic; their valence electrons are present either as bonding pairs or as unshared pairs. The principles involved in the bonding are similar to those in xenon fluorides and have been discussed in Chapter 3.

Chlorine trifluoride is a liquid (bp 11.8 °C) that is commercially available in tanks. It is made by direct combination at 200–300 °C. Reaction of ClF₃ with excess Cl₂ gives chlorine monofluoride, which is a gas (bp –100 °C).

Bromine trifluoride, a red liquid (bp 126 °C), is also made by direct interaction.

These three substances, which are typical of all halogen fluorides, are very reactive. They react explosively with H₂O and organic substances. They are powerful fluorinating agents for inorganic compounds, and when diluted with N₂, they fluorinate organic compounds.

Interhalogen ions can be either cations or anions. Halogen fluorides react with fluoride ion acceptors, for example,

\[ 2 \text{ClF} + \text{AsF}_5 = \text{FCI}_2\text{AsF}_5^- \]  

(20-6.1)

or with fluoride ion donors,

\[ \text{IF}_5 + \text{CsF} = \text{Cs}^+\text{IF}_6^- \]  

(20-6.2)
It is not always clear that such products contain discrete ions. For instance, in ClF₅SbF₆ each Cl atom has two close and two distant (belonging to SbF₆) fluorine neighbors in a much distorted square.

The pale yellow triiodide ion is formed on dissolving I₂ in aqueous KI. There are numerous salts of I⁻. Other ions are not usually stable in aqueous solution although they can be obtained in CH₃OH or CH₃CN and as crystalline salts of large cations such as Cs⁺ or R₄N⁺. For chlorine, the ion is formed only in concentrated solution.

\[
\text{Cl}^- (\text{aq}) + \text{Cl}_2 \rightleftharpoons \text{Cl}_3 (\text{aq}) \quad K \approx 0.2 \quad (20-6.3)
\]

The electrical conductance of molten I₂ is ascribed to self-ionization

\[
3 \text{I}_2 \rightleftharpoons \text{I}_3^- + \text{I}_3^+ \quad (20-6.4)
\]

20-7 Organic Compounds of Fluorine

Although the halogens form innumerable organic compounds, the methods of making organic fluorine compounds and some of their unusual properties are of interest in inorganic chemistry. Fluorination of other halogen compounds by treatment with metal fluorides has been discussed in Section 20-3. These methods are expensive so that alternative cheaper methods suitable for industrial procedures have been developed.

1. **Replacement of chlorine using hydrogen fluoride.** Anhydrous HF is cheap and can be used to replace Cl in chloro compounds. Catalysts such as SbCl₅ or CrF₄, and moderate temperature and pressure are required. Examples are

\[
2 \text{CCl}_4 + 3 \text{HF} \longrightarrow \text{CCl}_2\text{F}_2 + \text{CCl}_3\text{F} + 3 \text{HCl} \quad (20-7.1)
\]

\[
\text{CCl}_3\text{COCl}_3 + \text{HF} \rightarrow \text{CF}_3\text{COCF}_3 \quad (20-7.2)
\]

2. **Electrolytic replacement of hydrogen by fluorine.** One of the most important laboratory and industrial methods is the electrolysis of organic compounds in liquid HF at voltages (~4.5–6) below that required for the liberation of F₂. Steel cells with Ni anodes and steel cathodes are used. Fluorination occurs at the anode. Although many organic compounds give conducting solutions in liquid HF, a conductivity additive may be required. Examples of such fluorinations are

\[
\text{(C}_2\text{H}_5\text{)}_2\text{O} \longrightarrow \text{(C}_2\text{F}_5\text{)}_2\text{O} \quad (20-7.3)
\]

\[
\text{C}_8\text{H}_{18} \longrightarrow \text{C}_8\text{F}_{18} \quad (20-7.4)
\]

\[
\text{(CH}_3\text{)}_2\text{S} \longrightarrow \text{CF}_3\text{SF}_5 + \text{(CF}_3\text{)}_2\text{SF}_4 \quad (20-7.5)
\]

\[
\text{(C}_4\text{H}_9\text{)}_3\text{N} \longrightarrow \text{(C}_4\text{F}_9\text{)}_3\text{N} \quad (20-7.6)
\]

\[
\text{CH}_3\text{CO}_2\text{H} \longrightarrow \text{CF}_3\text{CO}_2\text{F} + \text{H}_2\text{O} \rightarrow \text{CF}_3\text{CO}_2\text{H} \quad (20-7.7)
\]

3. **Direct replacement of hydrogen by fluorine.** Although most organic compounds normally inflame or explode with fluorine, direct fluorination of many compounds is possible as follows.
(a) Catalytic fluorination where the reacting compound and F₂ diluted with N₂ are mixed in the presence of copper gauze or a cesium fluoride catalyst. An example is shown in Reaction 20-7.8.

\[ \text{C}_6\text{H}_6 + 9 \text{F}_2 \xrightarrow{\text{Cu}, 265\,\degree\text{C}} \text{C}_6\text{F}_{12} + 6 \text{HF} \quad (20-7.8) \]

(b) The reaction of the substrate in the solid state, over a long period of time with F₂ (diluted with He), at low temperature. It is important to allow heat, generated in the exothermic reaction (overall for replacement of H by F, \(-420\,\text{kJ mol}^{-1}\)), which could lead to C—C bond breaking, to be efficiently dissipated. The replacement reaction proceeds by several steps, each less exothermic than the C—C average bond strength, so that, provided the reaction time allows separate completion of individual steps, fluorination without degradation is possible. Examples of materials that can be fluorinated in this way are polystyrene, anthracene, phthalocyanine, carboranes, and so on.

(c) Inorganic fluorides, such as cobalt(III) fluoride, are used for the vapor-phase fluorination of organic compounds, for example,

\[ (\text{CH}_3)_3\text{N} \xrightarrow{\text{CoF}_3} (\text{CF}_3)_3\text{N} + (\text{CF}_3)_2\text{NF} + \text{CF}_3\text{NF}_2 + \text{NF}_3 \quad (20-7.9) \]

4. Other methods for fluorination. A useful and selective fluorinating agent for oxygen compounds is SF₄ (Section 19-4); for example, ketones RR'CO may be converted to RR'CF₂, and carboxylate groups CO₂H to CF₃.

Cesium fluoride acts as a catalyst in various fluorination reactions, for example,

\[ \text{R}_7\text{CN} + \text{F}_2 \xrightarrow{\text{CsF}, -78\,\degree\text{C}} \text{R}_7\text{CF}_2\text{NF}_2 \quad (\text{R}_7 = \text{perfluoralkyl}) \quad (20-7.10) \]

The F⁻ ion is very nucleophilic toward unsaturated fluorocarbons and adds to the positive center of a polarized multiple bond. The carbanion so produced may then undergo double-bond migration or may act as a nucleophile leading to the elimination of F⁻ or another ion by an S_N2 mechanism. Fluoride-initiated reactions of these types have wide scope. The reactions can be carried out in DMF or diglyme by using either the sparingly soluble CsF or the more soluble \((\text{C}_2\text{H}_5)_4\text{NF}\). An example is:

\[ \text{CF}_2=\text{CFCF}_3 \xrightarrow{\text{F}^-} (\text{CF}_3)_2\text{CF}^- \xrightarrow{\text{I}_2} (\text{CF}_3)_2\text{CFI}+\Gamma^- \quad (20-7.11) \]

Properties of Organofluorine Compounds

The C—F bond energy is very high (486 kJ mol⁻¹; cf. C—H 415, and C—Cl 332 kJ mol⁻¹), but organic fluorides are not necessarily particularly stable thermodynamically. The low reactivities of fluorine derivatives can be attributed to the impossibility of expansion of the octet of fluorine and the inability of, say, water to coordinate to fluorine or carbon as the first step in hydrolysis. With chlorine this may be possible using outer d orbitals. Because of the small size of the F atom, H can be replaced by F with the least amount of strain or distortion, as compared with replacement by other halogen atoms. The F atoms also effectively shield the
C atoms from attack. Finally, since C bonded to F can be considered to be effectively oxidized (whereas in C—H it is reduced), there is no tendency for oxidation by oxygen. Fluorocarbons are attacked only by hot metals, for example molten Na. When pyrolyzed, they split at C—C rather than C—F bonds.

The replacement of H by F leads to increased density, but less than by other halogens. Completely fluorinated (called perfluoro) derivatives, CₙF₂₊₂ , have very low boiling points for their molecular weights and low intermolecular forces; the weakness of these forces is also shown by the very low coefficient of friction for polytetrafluoroethylene, (CF₂—CF₂)ₙ.

Chlorofluorocarbons are used as nontoxic, inert refrigerants, aerosol bomb propellants, and heat-transfer agents. Fluoroolefins are used as monomers for free radical initiated polymerizations to give oils, greases, and the like, and also as chemical intermediates. The compound CF₃CHBrCI is a safe anaesthetic and the compound CHClF₂ is used for making tetrafluoroethylene.

\[
2 \text{CHClF}_2 \xrightarrow{500-1000 \degree C} \text{CF}_2=\text{CF}_2 + 2 \text{HCl}
\]  
(20-7.12)

Tetrafluoroethylene (bp -76.6 \degree C) can be polymerized thermally or in aqueous emulsion; the polymer is used for coating frying pans, resistant gaskets, and the like. Chlorofluorocarbons are now being phased out of use because they are photochemically decomposed in the upper atmosphere to give chlorine atoms, which catalyze ozone decomposition. Since destruction of any further significant percentage of this atmospheric ozone could have adverse effects, the problem of "ozone depletion" has been given serious study in recent years. It is not yet known to what extent permanent damage has already been done, nor is it clear what other events (namely, the increasing CO₂ and SO₂ concentrations in the atmosphere) will contribute to the complicated pattern of O₃ concentrations in the upper atmosphere.

Fluorinated carboxylic acids are strong acids. For example, CF₃CO₂H has \(K_a = 5.9 \times 10^{-1}\), while for the parent acetic acid, CH₃CO₂H, \(K_a = 1.8 \times 10^{-5}\). Many reactions of fluorocarboxylic acids leave the fluoroalkyl group intact. Consider, for example, the sequence of esterification by Reaction 20-7.13:

\[
\text{C}_3\text{F}_7\text{CO}_2\text{H} \xrightarrow{\text{H}_2\text{SO}_4} \text{C}_3\text{F}_7\text{CO}_2\text{C}_2\text{H}_5
\]  
(20-7.13)
ammonolysis according to Reaction 20-7.14:

\[
\text{C}_3\text{F}_7\text{CO}_2\text{C}_2\text{H}_5 \xrightarrow{\text{NH}_3} \text{C}_3\text{F}_7\text{CONH}_2
\]  
(20-7.14)
followed either by dehydration:

\[
\text{C}_3\text{F}_7\text{CONH}_2 \xrightarrow{\text{P}_2\text{O}_5} \text{C}_3\text{F}_7\text{CN}
\]  
(20-7.15)
or by reduction:

\[
\text{C}_3\text{F}_7\text{CONH}_2 \xrightarrow{\text{LiAlH}_4} \text{C}_3\text{F}_7\text{CH}_2\text{NH}_2
\]  
(20-7.16)
all of which leaves the fluoroalkyl group untouched.

Perfluoroalkyl halides are made by Reaction 20-7.17.

\[
\text{R}_F\text{CO}_2\text{Ag} + \text{I}_2 \xrightarrow{\text{heat}} \text{R}_F\text{I} + \text{CO}_2 + \text{AgI}
\]  
(20-7.17)
Perfluoroalkyl halides are relatively reactive, undergoing free radical reactions when heated or irradiated. Because of the very strong electron-withdrawing nature of perfluoroalkyl groups, they do not undergo most of the nucleophilic reactions typical of the alkyl halides. Trifluoromethyl iodide is readily cleaved homolytically according to Reaction 20-7.18:

$$\text{CF}_3\text{I} = \text{CF}_3^+ + \text{I}^- \quad \Delta H = 115 \text{ kJ mol}^{-1} \quad (20-7.18)$$

and radical reactions of CF$_3$I give CF$_3$ derivatives, an example being Reaction 20-7.19.

$$\text{CF}_3\text{I} + \text{P} \xrightarrow{\text{heat}} (\text{CF}_3)_n \text{P}_{3-n} \quad (20-7.19)$$

**STUDY GUIDE**

**Study Questions**

**A. Review**

1. Where, and in what chemical form, are the halogens found in nature?
2. How are the free halogens prepared from their halide salts?
3. List the main methods for the preparations of various anhydrous compounds of chlorine.
4. Give balanced equations for preparations of the following:
   (a) CrCl$_3$ from [Cr(H$_2$O)$_6$]Cl$_3$
   (b) FeCl$_3$ from Fe
   (c) PBr$_3$ from red P
   (d) CuI from aqueous CuSO$_4$
   (e) FeCl$_2$ from Fe
   (f) GdCl$_3$ from Gd$_2$O$_3$
5. Why is it impossible to make iodides of elements in high oxidation states, whereas corresponding bromides and chlorides are known?
6. Which elements give chlorides that are essentially insoluble in water or dilute HNO$_3$?
7. How may halides act as bridging ligands?
8. Give balanced equations for the preparations of the following oxo halogen compounds:
   (a) ClO$_2$
   (b) I$_2$O$_5$
   (c) NaOCl(aq)
   (d) NaClO$_2$
   (e) NaClO$_3$
   (f) NaClO$_4$
9. What are the general formulas and names of the four types of oxo acids of the halogens and their anions? In the case of iodine, there is one of unique stoichiometry. What is its formula?
10. Name one cationic, one neutral, and one anionic interhalogen compound. In those consisting of three or more atoms, state the rule that predicts which atom will be the central atom.
11. Iodine has a very low solubility in water, but dissolves readily in KI(aq). Why?
12. Describe two methods for making fluoroorganic compounds.
B. Additional Exercises

1. The compound F2O2 has a very short O—O bond (1.217 Å) compared with those in H2O2 (1.48 Å) and O2 (1.49 Å). It also has relatively long O—F bonds (1.575 Å) compared with those in OF2. Why?

2. ClO2 is a free radical with one unpaired electron, and it has less tendency to dimerize than does NO2. Why?

3. Suggest a geometry for SbF3 and SbCl5. Classify each Sb atom according to the ABxEy scheme of Chapter 3.

4. Draw the shapes of the following molecules and ions, giving the ABxEy classification and the hybridization for each central atom. (a) ClF (b) BrF3 (c) IF5 (d) IF7 (e) CIF4 (f) I5− (g) BrF4− (h) ICl4−

5. What is the order of acid strength for the following: HClO, HClO2, HClO3, and HClO4? Why?

6. Why can F2 not be obtained by electrolysis of aqueous solutions of NaF?

7. Predict the details of the structures of (a) O2F2 (b) ClO2 (c) BrO3− (d) H4IO6 (e) BrO4−

8. Write balanced equations for each of the following:
   (a) The oxidation of aqueous HCl by MnO2.
   (b) The oxidation of aqueous HI by MnO4.
   (c) Hydrolysis of SeF6.
   (d) Reduction of KClO3 by oxalic acid.
   (e) Reaction of aqueous barium chlorite with sulfuric acid.
   (f) Oxidation of Mn2+ to MnO4− by periodic acid.

9. How might you obtain CF3NO from CF3I?

10. An unknown metal carbonyl (1.86 g) was heated with excess iodine dissolved in pyridine, liberating CO. The gas was passed over I2O5, and the resulting I2 was extracted with CCl4. The amount of I2 in the CCl4 solution was determined by reaction with sodium thiosulfate, 20.0 mL of a 1.00 M solution being required. Write balanced equations for each step in the analysis, and calculate the formula of the unknown metal carbonyl.

11. Describe the bonding in I5 and I3.

12. Describe the three-center, four-electron (3c–4e) bond system of the molecular halide M2Cl10, Structure 20-II.

C. Problems from the Literature of Inorganic Chemistry

   (a) Perbromic acid in aqueous solution and alkali perbromates were shown to contain the same tetrahedral BrO4− ion. On what basis was this conclusion reached?
   (b) Periodates are rapidly hydrated to H4IO6. How was it demonstrated that this does not happen for perbromate?

   (a) How was the square planar geometry of IF4− established?
   (b) Discuss the geometries of IF4− and XeF4 in terms of VSEPR theory.

   (a) Discuss the structure in the solid state of [BrF4][Sb2F11] by taking the view that it
is constructed through Lewis acid-base interactions between [BrF⁺], [SbF₆⁻], and SbF₅. Identify all donor-acceptor interactions in Fig. 1 of this paper.

(b) What would be the geometries of [BrF⁺], [SbF₆⁻], and SbF₅ in the absence of these solid state interactions?

4. The compound CIF₃O was described in a series of papers by K. O. Christe et al., Inorg. Chem., 1972, 11, 2189, 2192, 2196, 2201, 2205, 2209, 2212.

(a) Write equations representing the synthesis of CIF₃O (i) from Cl₂O—note the precautions! (ii) from NaClO₂, and (iii) from ClONO₂.

(b) Write equations for the thermal decomposition of CIF₃, CIF₅, IOF₃, FCIO₂, and CIF₃O.

(c) What reactions may be used in photochemical syntheses of CIF₃O?

(d) What is the structure of CIF₃O? Classify it according to the AB₄Eₐ system.

(e) List two reactions in which CIF₃O serves as a Lewis acid.

(f) List two reactions in which CIF₃O serves as a Lewis base.

(g) What are the structures of the ions CIF₄O⁻ and CIF₂O⁺?


SUPPLEMENTARY READING


Supplementary Reading

