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 CaF_2 (*fluorspar*), Na_3AlF_6 (*cryolite*), and $3Ca_3(PO_4)_2Ca(F,Cl)_2$ (*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 F_2 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 (MHF_2).

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 O_2, He, Ne, and Kr. It also attacks many other com-

pounds, breaking them down to fluorides; organic materials often inflame and burn in F_2.

The great reactivity of F_2 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 H_2O_2 and N_2H_4.

Chlorine occurs as NaCl, KCl, $MgCl_2$, 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.

$$Na^+ + e^- = Na \tag{20-2.1}$$

$$Cl^- = \tfrac{1}{2}Cl_2 + e^- \tag{20-2.2}$$

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.

$$Cl_2 + H_2O = HCl + HOCl \tag{20-2.3}$$

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

$$2\,Br^- + Cl_2 \xrightarrow{\;pH \sim 3.5\;} 2\,Cl^- + Br_2 \tag{20-2.4}$$

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 CS_2 and CCl_4.

Iodine occurs as iodide in brines and as iodate in Chile saltpeter (guano, $NaNO_3$). Various forms of marine life concentrate iodine. Production of I_2 involves either oxidizing I^- or reducing iodates to I^- followed by oxidation. An acid solution of MnO_2 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 CS_2 and CCl_4. Such solutions are purple, as is the vapor. In polar solvents, unsaturated hydrocarbons, and liquid SO_2, brown or pinkish-brown solutions are formed. These colors indicate the formation of weak complexes $I_2 \cdots S$ known as *charge-transfer complexes*. The bonding energy results from partial transfer of charge in the sense $I_2^- S^+$. The complexes of I_2 and also of Br_2, Cl_2, 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 I_5^- 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 $^{209}Bi(\alpha,2n)^{211}At$ 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, CH_3At, 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 C_6H_5At, $C_6H_5AtCl_2$, and $C_6H_5AtO_2$ are known.
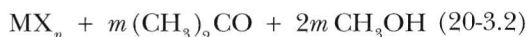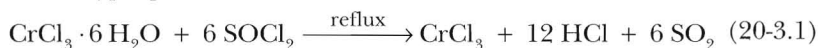
20-3 Halides

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 $VOCl_3$, 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.
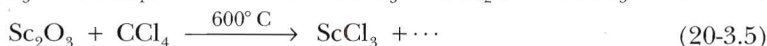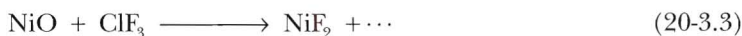
Direct fluorination normally gives fluorides in the higher oxidation states. Most metals and nonmetals react very vigorously with F_2; with nonmetals such as P_4, the reaction may be explosive. For rapid formation in dry reactions of *chlorides, bromides,* and *iodides* elevated temperatures are usually necessary. For metals, the reaction with Cl_2 and Br_2 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.

$$CrCl_3 \cdot 6\,H_2O + 6\,SOCl_2 \xrightarrow{\text{reflux}} CrCl_3 + 12\,HCl + 6\,SO_2 \quad (20\text{-}3.1)$$

$$MX_n \cdot m\,H_2O \text{ in } CH_3C(OCH_3)_2CH_3 \longrightarrow$$
$$MX_n + m\,(CH_3)_2CO + 2m\,CH_3OH \quad (20\text{-}3.2)$$

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:

$$NiO + ClF_3 \longrightarrow NiF_2 + \cdots \quad (20\text{-}3.3)$$

$$Pr_2O_3 + 6\,NH_4Cl \xrightarrow{300°\,C} 3\,PrCl_3 + 3\,H_2O + 6\,NH_3 \quad (20\text{-}3.4)$$

$$Sc_2O_3 + CCl_4 \xrightarrow{600°\,C} ScCl_3 + \cdots \quad (20\text{-}3.5)$$

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 CoF_3 or AsF_5. 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 SbF_3, which is used along with $SbCl_5$ as a catalyst in Reaction 20-3.6.

$$C_6H_5CCl_3 + SbF_3 \longrightarrow C_6H_5CF_3 + SbCl_3 \qquad (20\text{-}3.6)$$

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-I, 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 BeF_2 there are infinite chains, – – – BeF_2BeF_2– – –, with bent bridges, similar to the situation in $BeCl_2$. 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.
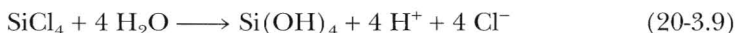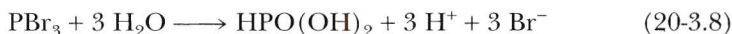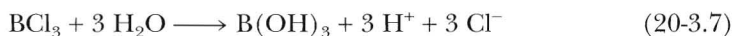

20-I   20-II   20-III
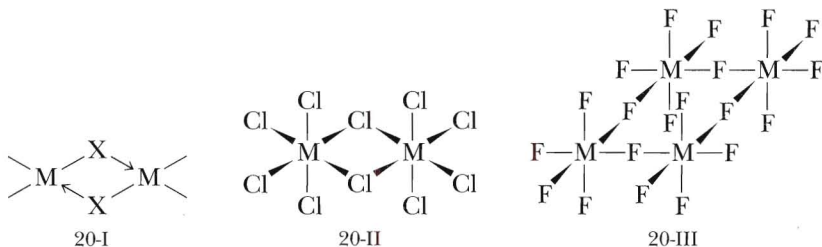
Molecular fluorides of both metals and nonmetals are usually gases or volatile liquids. Their volatility is due to the absence of intermolecular bonding other

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, SF_6, 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 F_2 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) CF_3CO_2H is a strong acid; (b) $(CF_3)_3N$ and NF_3 have no basicity; and (c) CF_3 derivatives in general are attacked much less readily by electrophilic reagents in anionic substitutions than are CH_3 compounds. The CF_3 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,

$$BCl_3 + 3\ H_2O \longrightarrow B(OH)_3 + 3\ H^+ + 3\ Cl^- \qquad (20\text{-}3.7)$$

$$PBr_3 + 3\ H_2O \longrightarrow HPO(OH)_2 + 3\ H^+ + 3\ Br^- \qquad (20\text{-}3.8)$$

$$SiCl_4 + 4\ H_2O \longrightarrow Si(OH)_4 + 4\ H^+ + 4\ Cl^- \qquad (20\text{-}3.9)$$

Where the maximum covalency is attained, as in CCl_4 or SF_6, the halides may be quite inert towards water. However, this is a result of kinetic and not thermodynamic factors. For instance, for CF_4, the equilibrium for hydrolysis, as in Reaction 20-3.10

$$CF_4(g) + 2\ H_2O(\ell) = CO_2(g) + 4\ HF(g) \qquad (20\text{-}3.10)$$
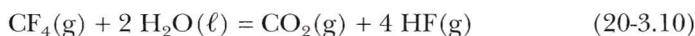
is thermodynamically favorable ($K_{eq} = 10^{23}$), but the rate of hydrolysis is negligible because there is no site for attack by water at carbon. The necessity for means of attack is also illustrated by the fact that SF_6 is not hydrolyzed, whereas SeF_6 and TeF_6 are hydrolyzed at 25 °C. Attack 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 (OF_2) is obtained as a pale yellow gas on passing F_2 gas rapidly through a 2% NaOH solution. Dioxygen difluoride (O_2F_2) is an unstable orange-yellow solid made by the action of electric discharges on F_2–O_2 mixtures; O_2F_2 is an extremely potent oxidizing and fluorinating agent.

Chlorine oxides are reactive, and tend to explode. None can be obtained by direct reaction of Cl_2 and O_2. The *dioxide* (ClO_2) is a powerful oxidant and is used diluted with air commercially, for example, for bleaching wood pulp. It is always
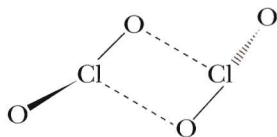
made "on site" by Reaction 20-4.1

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

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.

20-IV   20-V

The compound Cl_2O 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 dehydration of iodic acid at elevated temperatures, as in Reaction 20-4.2.

$$2 \text{ HIO}_3 \underset{\substack{\text{H}_2\text{O} \\ \text{fast}}}{\overset{240\ °\text{C}}{\rightleftharpoons}} \text{I}_2\text{O}_5 + \text{H}_2\text{O} \qquad (20\text{-}4.2)$$

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

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

where the liberated iodine is determined by iodometry. Iodine pentoxide has a three-dimensional network structure with O_2I—O—IO_2 units linked by strong intermolecular $\text{I} \cdots \text{O}$ 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_2O 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*.

$$\text{X}_2(\text{g,}\ell\text{,s}) = \text{X}_2(\text{aq}) \qquad\qquad K_1 \qquad\qquad (20\text{-}5.1)$$

$$\text{X}_2(\text{aq}) = \text{H}^+ + \text{X}^- + \text{HOX} \qquad K_2 \qquad\qquad (20\text{-}5.2)$$

Table 20-1   Standard Potentials (in V) for Reactions of Halogen Compounds

Reaction	Cl	Br	I
(1) $H^+ + HOX + e^- = \frac{1}{2} X_2(g,\ell,s) + H_2O$	1.63	1.59	1.45
(2) $3 H^+ + HXO_2 + 3 e^- = \frac{1}{2} X_2 (g,\ell,s) + 2 H_2O$	1.64		
(3) $6 H^+ + XO_3^- + 5 e^- = \frac{1}{2} X_2(g,\ell,s) + 3 H_2O$	1.47	1.52	1.20
(4) $8 H^+ + XO_4^- + 7 e^- = \frac{1}{2} X_2(g,\ell,s) + 4 H_2O$	1.42	1.59	1.34
(5) $\frac{1}{2} X_2(g,\ell,s) + e^- = X^-$	1.36	1.07	0.54[a]
(6) $XO^- + H_2O + 2 e^- = X^- + 2 OH^-$	0.89	0.76	0.49
(7) $XO_2^- + 2 H_2O + 4 e^- = X^- + 4 OH^-$	0.78		
(8) $XO_3^- + 3 H_2O + 6 e^- = X^- + 6 OH^-$	0.63	0.61	0.26
(9) $XO_4^- + 4 H_2O + 8 e^- = X^- + 8 OH^-$	0.56	0.69	0.39

[a]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 4.2×10^{-4} for Cl_2, 7.2×10^{-9} for Br_2, and 2.0×10^{-13} for I_2. We can also estimate from

$$\frac{1}{2} X_2 + e^- = X^- \tag{20-5.3}$$

and

$$O_2 + 4 H^+ + 4 e^- = 2 H_2O \qquad E^\circ = 1.23 \text{ V} \tag{20-5.4}$$

that the potentials for the reactions

$$2 H^+ + 2 X^- + \frac{1}{2} O_2 = X_2 + H_2O \tag{20-5.5}$$

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})

	Cl_2	Br_2	I_2
Total solubility	0.091	0.21	0.0013
Concentration X_2(aq), (mol L^{-1})	0.061	0.21	0.0013
$[H^+] = [X^-] = [HOX]$	0.030	1.15×10^{-3}	6.4×10^{-6}

also unstable. They are known only in solution from the interaction of the halogen and Hg^{II} oxide.

$$2 X_2 + 2 HgO + H_2O \longrightarrow HgO \cdot HgX_2 + 2 HOX \qquad (20\text{-}5.6)$$

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

$$X_2 + 2 OH^- \longrightarrow XO^- + X^- + H_2O \qquad (20\text{-}5.7)$$
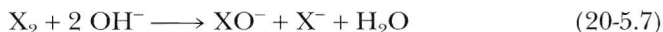
and for these *rapid* reactions the equilibrium constants are all favorable: 7.5×10^{15} for Cl_2, 2×10^8 for Br_2, and 30 for I_2.

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

$$3 XO^- = 2 X^- + XO_3^- \qquad (20\text{-}5.8)$$

For these reactions, the equilibrium constants are very favorable: 10^{27} for ClO^-, 10^{15} for BrO^-, and 10^{20} for IO^-. 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^- is slow at and below room temperature. Thus, when Cl_2 reacts with base "in the cold," reasonably pure solutions of Cl^- and ClO^- are obtained. In hot solutions ($\sim 75\ °C$) the rate of disproportionation is fairly rapid and good yields of ClO_3^- can be secured.

The disproportionation of BrO^- is moderately fast even at room temperature. Solutions of BrO^- can only be made and/or kept at around $0\ °C$. At temperatures of 50–$80\ °C$ quantitative yields of BrO_3^- are obtained.

$$3 Br_2 + 6 OH^- \longrightarrow 5 Br^- + BrO_3^- + 3 H_2O \qquad (20\text{-}5.9)$$

The rate of disproportionation of IO^- is so fast that it is unknown in solution. Hence, reaction of I_2 with base gives IO_3^- quantitatively according to an equation analogous to that for Br_2.

Halous Acids

The only certain acid is *chlorous acid* ($HClO_2$). This acid is obtained in aqueous solution by treating a suspension of barium chlorite with H_2SO_4, and filtering off the $BaSO_4$. It is a relatively weak acid ($K_a \approx 10^{-2}$) and cannot be isolated. *Chlorites* ($MClO_2$) are obtained by reaction of ClO_2 with solutions of bases.

$$2 ClO_2 + 2 OH^- \longrightarrow ClO_2^- + ClO_3^- + H_2O \qquad (20\text{-}5.10)$$

Chlorites are used as bleaching agents. In alkaline solution ClO_2^- is quite stable even on boiling. In acid solutions, the decomposition is rapid and is catalyzed by Cl^-.

$$5 \text{ HClO}_2 \longrightarrow 4 \text{ ClO}_2 + \text{Cl}^- + \text{H}^+ + 2 \text{ H}_2\text{O} \qquad (20\text{-}5.11)$$
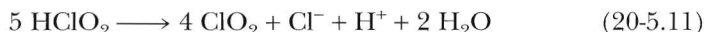
Halic Acids

Iodic acid, HIO_3, is a stable white solid obtained by oxidizing I_2 with concentrated HNO_3, H_2O_2, O_3, and so on. *Chloric* and *bromic acids* are obtained in solution by treating the barium halates with H_2SO_4.

The halic acids are strong acids and are powerful oxidizing agents. The ions 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 AB_3E 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 ClO_3^- is thermodynamically very favorable,

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

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 BrO_3^- to BrO_4^- and Br^- is extremely unfavorable ($K \sim 10^{-33}$). *Perbromates* can be obtained only by oxidation of BrO_3^-, preferably by F_2, in basic solution.
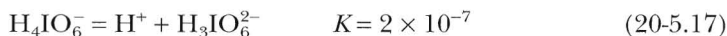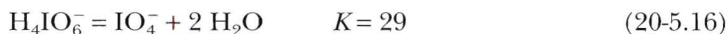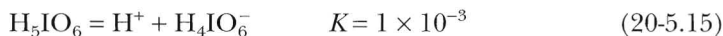
$$\text{BrO}_3^- + \text{F}_2 + 2 \text{ OH}^- = \text{BrO}_4^- + 2 \text{ F}^- + \text{H}_2\text{O} \qquad (20\text{-}5.13)$$
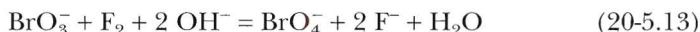
The perbromates are exceedingly powerful oxidants.

$$\text{BrO}_4^- + 2 \text{ H}^+ + 2 \text{ e}^- = \text{BrO}_3^- + \text{H}_2\text{O} \qquad E° = +1.76 \text{ V} \qquad (20\text{-}5.14)$$

Solutions of 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

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

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

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

In aqueous solutions at 25 °C the main ion is IO_4^-. The pH-dependent equilibria are established rapidly. Kinetic studies of the hydration of 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 Mn^{2+} to MnO_4^-.
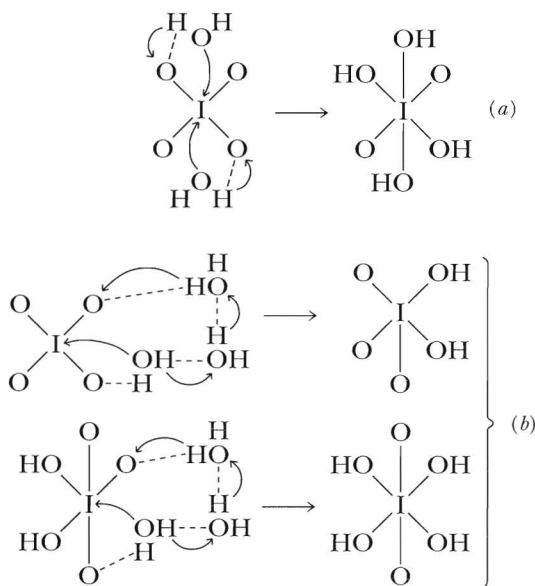
Figure 20-1   Schematic representation of (a) the one-step and (b) the two-step mechanism for the aquation of IO_4^- to $IO_2(OH)_4^-$. Dotted lines represent hydrogen bonds.

20-6 Interhalogen Compounds

The halogens form many compounds among themselves in binary combinations that may be neutral or ionic (e.g., BrCl, IF_5, Br_3^+, I_3^-). *Ternary* combinations occur only in polyhalide ions (e.g., $IBrCl^-$).

Neutral interhalogen compounds are of the type XX'_n, 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 ClF_3 with excess Cl_2 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 H_2O and organic substances. They are powerful fluorinating agents for inorganic compounds, and when diluted with N_2, they fluorinate organic compounds.

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

$$2\ ClF + AsF_5 = FCl_2^+ AsF_6^- \tag{20-6.1}$$

or with fluoride ion donors,

$$IF_5 + CsF = Cs^+ IF_6^- \tag{20-6.2}$$

It is not always clear that such products contain *discrete* ions. For instance, in $ClF_2^+SbF_6^-$ each Cl atom has two close and two distant (belonging to SbF_6^-) fluorine neighbors in a much distorted square.

The pale yellow *triiodide* ion is formed on dissolving I_2 in aqueous KI. There are numerous salts of I_3^-. Other ions are not usually stable in aqueous solution although they can be obtained in CH_3OH or CH_3CN and as crystalline salts of large cations such as Cs^+ or R_4N^+. For chlorine, the ion is formed only in concentrated solution.

$$Cl^-(aq) + Cl_2 \rightleftharpoons Cl_3^-(aq) \qquad K \approx 0.2 \qquad (20\text{-}6.3)$$

The electrical conductance of molten I_2 is ascribed to self-ionization

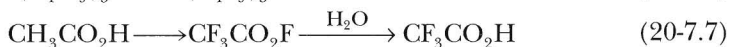$$3\,I_2 \rightleftharpoons I_3^+ + I_3^- \qquad (20\text{-}6.4)$$

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 $SbCl_5$ or CrF_4, and moderate temperature and pressure are required. Examples are

$$2\,CCl_4 + 3\,HF \longrightarrow CCl_2F_2 + CCl_3F + 3\,HCl \qquad (20\text{-}7.1)$$

$$CCl_3COCCl_3 \xrightarrow{\ HF\ } CF_3COCF_3 \qquad (20\text{-}7.2)$$

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 F_2. 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

$$(C_2H_5)_2O \longrightarrow (C_2F_5)_2O \qquad (20\text{-}7.3)$$

$$C_8H_{18} \longrightarrow C_8F_{18} \qquad (20\text{-}7.4)$$

$$(CH_3)_2S \longrightarrow CF_3SF_5 + (CF_3)_2SF_4 \qquad (20\text{-}7.5)$$

$$(C_4H_9)_3N \longrightarrow (C_4F_9)_3N \qquad (20\text{-}7.6)$$

$$CH_3CO_2H \longrightarrow CF_3CO_2F \xrightarrow{\ H_2O\ } CF_3CO_2H \qquad (20\text{-}7.7)$$

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 F_2 diluted with N_2 are mixed *in the presence* of copper gauze or a cesium fluoride catalyst. An example is shown in Reaction 20-7.8.

$$C_6H_6 + 9\ F_2 \xrightarrow{\text{Cu, 265 °C}} C_6F_{12} + 6\ HF \qquad (20\text{-}7.8)$$
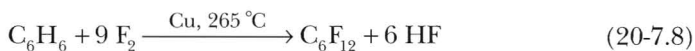
(b) The reaction of the substrate in the solid state, over a long period of time with F_2 (diluted with He), at low temperature. It is important to allow heat, generated in the exothermic reaction (overall for replacement of H by F, $\sim 420\ kJ\ mol^{-1}$), which could lead to C—C bond breaking, to 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,

$$(CH_3)_3N \xrightarrow{\text{CoF}_3} (CF_3)_3N + (CF_3)_2NF + CF_3NF_2 + NF_3 \qquad (20\text{-}7.9)$$
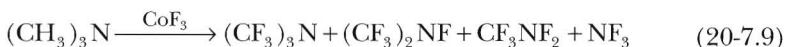
4. Other methods for fluorination. A useful and selective fluorinating agent for oxygen compounds is SF_4 (Section 19-4); for example, ketones $RR'CO$ may be converted to $RR'CF_2$, and carboxylate groups CO_2H to CF_3.

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

$$R_FCN + F_2 \xrightarrow{\text{CsF, }-78\ °C} R_FCF_2NF_2 \qquad (R_F = \text{perfluoralkyl}) \quad (20\text{-}7.10)$$

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 $(C_2H_5)_4NF$.

An example is:

$$CF_2\!\!=\!\!CFCF_3 \xrightarrow{F^-} (CF_3)_2CF^- \xrightarrow{I_2} (CF_3)_2CFI + I^- \qquad (20\text{-}7.11)$$
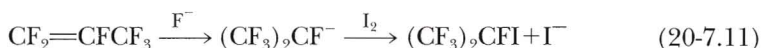
Properties of Organofluorine Compounds

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, C_nF_{2n+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, $(CF_2—CF_2)_n$.

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 $CF_3CHBrCl$ is a safe anaesthetic and the compound $CHClF_2$ is used for making tetrafluoroethylene.

$$2\ CHClF_2 \xrightarrow{500-1000\ °C} CF_2{=}CF_2 + 2\ HCl \qquad (20\text{-}7.12)$$

Tetrafluoroethylene (bp $-76.6\ °C$) 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 CO_2 and SO_2 concentrations in the atmosphere) will contribute to the complicated pattern of O_3 concentrations in the upper atmosphere.

Fluorinated carboxylic acids are strong acids. For example, CF_3CO_2H has $K_a = 5.9 \times 10^{-1}$, while for the parent acetic acid, CH_3CO_2H, $K_a = 1.8 \times 10^{-5}$. Many reactions of fluorocarboxylic acids leave the fluoroalkyl group intact. Consider, for example, the sequence of esterification by Reaction 20-7.13:

$$C_3F_7CO_2H \xrightarrow[C_2H_5OH]{H_2SO_4} C_3F_7CO_2C_2H_5 \qquad (20\text{-}7.13)$$

ammonolysis according to Reaction 20-7.14:

$$C_3F_7CO_2C_2H_5 \xrightarrow{NH_3} C_3F_7CONH_2 \qquad (20\text{-}7.14)$$

followed either by dehydration:

$$C_3F_7CONH_2 \xrightarrow{P_2O_5} C_3F_7CN \qquad (20\text{-}7.15)$$

or by reduction:

$$C_3F_7CONH_2 \xrightarrow{LiAlH_4} C_3F_7CH_2NH_2 \qquad (20\text{-}7.16)$$

all of which leaves the fluoroalkyl group untouched.

Perfluoroalkyl halides are made by Reaction 20-7.17.

$$R_FCO_2Ag + I_2 \xrightarrow{heat} R_FI + CO_2 + AgI \qquad (20\text{-}7.17)$$
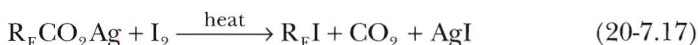
Perfluoroalkyl halides are relatively reactive, undergoing free radical reactions when heated or irradiated. Because of the very strong electron-withdrawing nature of perfluoroalkyl groups, they do not undergo most of the nucleophilic reactions typical of the alkyl halides. Trifluoromethyl iodide is readily cleaved homolytically according to Reaction 20-7.18:

$$CF_3I = CF_3^{\cdot} + I^{\cdot} \qquad \Delta H = 115 \text{ kJ mol}^{-1} \qquad (20\text{-}7.18)$$
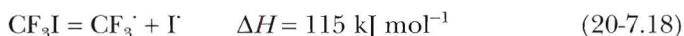
and radical reactions of CF_3I give CF_3 derivatives, an example being Reaction 20-7.19.

$$CF_3I + P \xrightarrow{\text{heat}} (CF_3)_n PI_{3-n} \qquad (20\text{-}7.19)$$
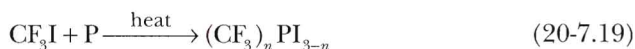
STUDY GUIDE

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 $[Cr(H_2O)_6]Cl_3$
   (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_2O_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_2O_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 F_2O_2 has a very short O—O bond (1.217 Å) compared with those in H_2O_2 (1.48 Å) and O_2^{2-} (1.49 Å). It also has relatively long O—F bonds (1.575 Å) compared with those in OF_2. Why?

2. ClO_2 is a free radical with one unpaired electron, and it has less tendency to dimerize than does NO_2. Why?

3. Suggest a geometry for SbF_3 and $SbCl_5$. Classify each Sb atom according to the AB_xE_y scheme of Chapter 3.

4. Draw the shapes of the following molecules and ions, giving the AB_xE_y classification and the hybridization for each central atom. (a) ClF   (b) BrF_3 (c) IF_5 (d) IF_7 (e) ClF_4^- (f) I_3^- (g) BrF_4^+ (h) ICl_2^+

5. What is the order of acid strength for the following: HClO, $HClO_2$, $HClO_3$, and $HClO_4$? Why?

6. Why can F_2 not be obtained by electrolysis of aqueous solutions of NaF?

7. Predict the details of the structures of (a) O_2F_2 (b) ClO_2 (c) BrO_3^- (d) $H_4IO_6^-$ (e) BrO_4^-

8. Write balanced equations for each of the following:
   (a) The oxidation of aqueous HCl by MnO_2.
   (b) The oxidation of aqueous HI by MnO_4^-.
   (c) Hydrolysis of SeF_6.
   (d) Reduction of $KClO_3$ by oxalic acid.
   (e) Reaction of aqueous barium chlorite with sulfuric acid.
   (f) Oxidation of Mn^{2+} to MnO_4^- by periodic acid.

9. How might you obtain CF_3NO from CF_3I?

10. An unknown metal carbonyl (1.86 g) was heated with excess iodine dissolved in pyridine, liberating CO. The gas was passed over I_2O_5, and the resulting I_2 was extracted with CCl_4. The amount of I_2 in the CCl_4 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 I_3^- and I_3^+.

12. Describe the three-center, four-electron (3c–4e) bond system of the molecular halide M_2Cl_{10}, Structure 20-II.

C. Problems from the Literature of Inorganic Chemistry

1. Consider the properties of the perbromate ion as reported by E. H. Appleman, *Inorg. Chem.*, **1969**, *8*, 223–227.
   (a) Perbromic acid in aqueous solution and alkali perbromates were shown to contain the same tetrahedral BrO_4^- ion. On what basis was this conclusion reached?
   (b) Periodates are rapidly hydrated to H_4IO_6. How was it demonstrated that this does not happen for perbromate?

2. The IF_4^- ion is featured in the work by K. O. Christe and D. Nauman, *Inorg, Chem.*, **1973**, *12*, 59–62.
   (a) How was the square planar geometry of IF_4^- established?
   (b) Discuss the geometries of IF_4^- and XeF_4 in terms of VSEPR theory.

3. The BrF_4^+ cation was studied by M. D. Lind and K. O. Christe, *Inorg. Chem.*, **1972**, *11*, 608–612.
   (a) Discuss the structure in the solid state of $[BrF_4^+][Sb_2F_{11}^-]$ by taking the view that it

is constructed through Lewis acid-base interactions between $[BrF_4^+]$, $[SbF_6^-]$, and SbF_5. Identify all donor–acceptor interactions in Fig. 1 of this paper.

(b) What would be the geometries of $[BrF_4^+]$, $[SbF_6^-]$, and SbF_5 in the absence of these solid state interactions?

4. The compound ClF_3O 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 ClF_3O (i) from Cl_2O—note the precautions! (ii) from $NaClO_2$, and (iii) from $ClONO_2$.

(b) Write equations for the thermal decomposition of ClF_3, ClF_5, IOF_5, $FClO_2$, and ClF_3O.

(c) What reactions may be used in photochemical syntheses of ClF_3O?

(d) What is the structure of ClF_3O? Classify it according to the AB_xE_y system.

(e) List two reactions in which ClF_3O serves as a Lewis acid.

(f) List two reactions in which ClF_3O serves as a Lewis base.

(g) What are the structures of the ions ClF_4O^- and ClF_2O^+?

5. Make a list of all of the reasons given recently by Gillespie and Robinson (R. J. Gillespie and E. A. Robinson, *Inorg. Chem.*, **1992**, *31*, 1960–1963) for proposing a new value (0.54 Å) for the covalent radius of fluorine.

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