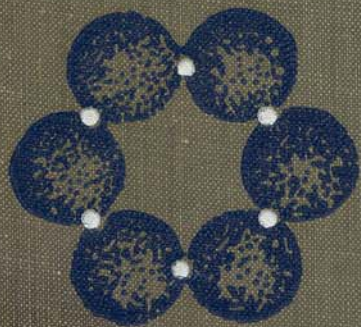*Linus Pauling*

COLLEGE
CHEMISTRY

Chapter 13

The Halogens

The halogens, fluorine, chlorine, bromine, and iodine, are the elements that immediately precede the noble gases in the periodic table. Their neutral atoms, with the electronic structures given in Table 13-1, have one electron less than the corresponding noble gas. They have a strong tendency to assume the electronic structure of the noble gas, either by adding an electron, to form a halogenide ion, as was discussed in Chapter 10, or by sharing an electron pair with another atom, forming a covalent bond (Chapters 7 and 11).

TABLE 13-1 *Electronic Structure of the Halogens*

Z	ELEMENT	K	L		M			N			O	
		1s	2s	2p	3s	3p	3d	4s	4p	4d	5s	5p
9	Fluorine	2	2	5								
17	Chlorine	2	2	6	2	5						
35	Bromine	2	2	6	2	6	10	2	5			
53	Iodine	2	2	6	2	6	10	2	6	10	2	5

Sometimes more than one electron pair is shared by a halogen atom with other atoms, especially atoms of oxygen. The oxygen compounds of the halogens are important substances. A few of them, such as potassium chlorate, have been mentioned in earlier chapters. The chemistry of these substances is complex, but it can be systematized and clarified by correlation with the electronic theory of valence.

13-1. *The Oxidation States of the Halogens*

The oxidation states which are represented by known compounds of the halogens are shown in the diagram on the following page. It is seen that the range of the oxidation states extends from −1, corresponding

to the achievement for each halogen atom of the structure of the adjacent noble gas, to $+7$, corresponding for chlorine to the inner noble-gas structure (neon). In general the odd oxidation states are represented by compounds. The importance of the odd oxidation states is the result of the stability of electronic structures involving pairs of electrons, either shared or unshared. Structures involving only pairs of electrons lead to even oxidation states for elements in even groups of the periodic system and to odd oxidation states for elements in odd groups. The exceptional compounds chlorine dioxide, ClO_2, bromine dioxide, BrO_2, and iodine dioxide, IO_2, corresponding to oxidation number $+4$, have molecules containing an odd number of electrons.

$+7$		$HClO_4$, Cl_2O_7		H_5IO_6
$+6$		Cl_2O_6		
$+5$		$HClO_3$	$HBrO_3$	HIO_3, I_2O_5
$+4$		ClO_2	BrO_2	IO_2
$+3$		$HClO_2$		
$+2$				
$+1$		$HClO$, Cl_2O	$HBrO$, Br_2O	HIO
0	F_2	Cl_2	Br_2	I_2
-1	HF, F^-	HCl, Cl^-	HBr, Br^-	HI, I^-

Fluorine differs significantly from the other halogens. Whereas chlorine, bromine, and iodine form many compounds with oxygen, fluorine forms very few. There are no oxygen acids of fluorine.

This fact can be correlated with the position of fluorine in the electronegativity scale (Section 11–8). Fluorine, with electronegativity 4.0, is the most electronegative of the elements. It is more electronegative than oxygen (electronegativity 3.5), whereas the other halogens (chlorine 3.0, bromine 2.8, iodine 2.5) are less electronegative than oxygen. The large electronegativity of fluorine causes instability of positive oxidation states of fluorine, and great stability of its negative oxidation state.

Fluorine forms one compound with oxygen, OF_2. It is produced by

reaction of fluorine with water. Its electronic structure is $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:$, and

it is considered to contain fluorine with oxidation number -1, because the electronegativity of fluorine is greater than that of oxygen; it is hence called *oxygen fluoride*, rather than fluorine oxide.

Illustrative Exercises

13-1.   Write the equation for the reaction of fluorine with water, producing oxygen fluoride. What is the other product of the reaction?

13-2.   What are the oxidation numbers of hydrogen, oxygen, and fluorine in the reactants and the products of the reaction of Exercise 13-1? What is the oxidizing agent in this reaction? What has been oxidized?

13-3.   How many liters of oxygen fluoride could be prepared by reaction of 10 l of fluorine with water?

13–2. *The Halogens and Halogenides*

The halogens consist of diatomic molecules, F_2, Cl_2, Br_2, and I_2. Some physical properties of the halogens are given in Table 13-2.

Fluorine.   Fluorine, the lightest of the halogens, is the most reactive of all the elements, and it forms compounds with all the elements except the inert gases. Substances such as wood and rubber burst into flame when held in a stream of fluorine, and even asbestos (a silicate of magnesium and aluminum) reacts vigorously with it and becomes incandescent. Platinum is attacked only slowly by fluorine. Copper and steel can be used as containers for the gas; they are attacked by it, but become coated with a thin layer of copper fluoride or iron fluoride which then protects them against further attack.

Fluorine was first made in 1886 by the French chemist Henri Moissan (1852–1907), by the method described in the following section. In recent years methods for its commercial production and transport (in steel tanks) have been developed, and it is now used in chemical industry in moderate quantities.

TABLE 13-2   *Properties of the Halogens*

| FORMULA		ATOMIC NUMBER	ATOMIC WEIGHT	COLOR AND FORM	MELTING POINT	BOILING POINT	IONIC RADIUS*
Fluorine	F_2	9	19.00	Pale yellow gas	−223° C	−187° C	1.36 Å
Chlorine	Cl_2	17	35.457	Greenish yellow gas	−101.6°	−34.6°	1.81
Bromine	Br_2	35	79.916	Reddish brown liquid	−7.3°	58.7°	1.95
Iodine	I_2	53	126.91	Grayish black lustrous solid	113.5°	184°	2.16

* For negatively charged ion with ligancy 6, such as Cl^- in the NaCl crystal.

Fluorine occurs in nature in the combined state in minerals such as *fluorite*, CaF_2; *fluor-apatite*, $Ca_5(PO_4)_3F$, which is a constituent of bones

and teeth; and *cryolite*, Na_3AlF_6; and in small quantities in sea water and most supplies of drinking water, as fluoride ion. If there is not a sufficient (very small) quantity of fluoride ion in the drinking water of children their teeth will not be properly resistant to decay.

The name fluorine, from Latin *fluere*, to flow, refers to the use of fluorite as a flux (a material that forms a melt with metal oxides).

Hydrogen fluoride, HF, can be made by treating fluorite with sulfuric acid:

$$H_2SO_4 + CaF_2 \longrightarrow CaSO_4 + 2HF \uparrow$$
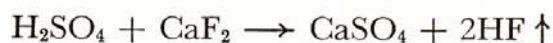
This method is used industrially. The reaction is usually carried out in the laboratory in a lead dish, because hydrogen fluoride attacks glass, porcelain, and other silicates. It is a colorless gas (m.p. $-92.3°$ C, b.p. $19.4°$ C), very soluble in water.

The solution of hydrogen fluoride in water is called hydrofluoric acid. This solution, and also hydrogen fluoride gas, may be used for etching glass.* The glass is covered with a thin layer of paraffin, through which the design to be etched, such as the graduations on a buret, is scratched with a stylus. The object is then treated with the acid. The reactions that occur are similar to those for quartz, SiO_2:

$$SiO_2 + 4HF \longrightarrow SiF_4 \uparrow + 2H_2O$$
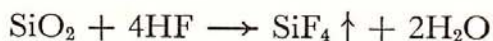
The product, SiF_4, silicon tetrafluoride, is a gas.

Hydrofluoric acid must be handled with great care, because on contact with the skin it produces sores which heal very slowly. The acid is stored in bottles made of polyethylene (a resistant plastic).

The salts of hydrofluoric acid are called fluorides. Sodium fluoride, NaF, is used as an insecticide.

Chlorine. Chlorine (from Greek *chloros*, greenish-yellow), the most common of the halogens, is a greenish-yellow gas, with a sharp irritating odor. It was first made by the Swedish chemist K. W. Scheele (1742–1786) in 1774, by the action of manganese dioxide on hydrochloric acid. It is now manufactured on a large scale by the electrolysis of a strong solution of sodium chloride.

Chlorine is a very reactive substance, but less reactive than fluorine. It combines with most elements, to form chlorides, at room temperature or on gentle heating. Hydrogen burns in chlorine, after being ignited, to form hydrogen chloride:

$$H_2 + Cl_2 \longrightarrow 2HCl$$
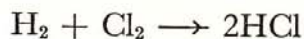
Iron burns in chlorine, producing ferric chloride, a brown solid,

_____

* Metals, such as copper, may be etched with nitric acid. Nitric acid and other acids, except hydrofluoric acid, do not attack glass.

$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3$$
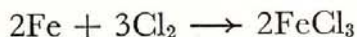
and other metals react similarly with it.

Chlorine is a strong oxidizing agent, and because of this property it is effective in killing bacteria. It is used extensively to sterilize drinking water, and is also used in many ways throughout the chemical industry.

Hydrogen chloride, HCl, is a colorless gas (m.p. $-112°$ C, b.p. $-83.7°$ C) with an unpleasant sharp odor. It is easily made by heating sodium chloride with sulfuric acid:

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl \uparrow$$
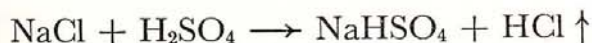
The gas dissolves readily in water, with the evolution of a large amount of heat. The solution is called hydrochloric acid. Hydrochloric acid is a strong acid—it has a very acidic taste, turns blue litmus paper red, dissolves zinc and other active metals with the evolution of hydrogen gas, and combines with bases to form salts. The salts formed by hydrochloric acid are called chlorides. A representative chloride is sodium chloride, which has been mentioned often in the preceding chapters; other chlorides will be discussed in later sections of the book.

Bromine. The element bromine (from Greek *bromos*, stench) occurs in the form of compounds in small quantities in sea water and in natural salt deposits. It is an easily volatile, dark reddish-brown liquid with a strong, disagreeable odor and an irritating effect on the eyes and throat. It produces painful sores when spilled on the skin. The free element can be made by treating a bromide with an oxidizing agent, such as chlorine.

Hydrogen bromide, HBr, is a colorless gas (m.p. $-88.5°$ C, b.p. $-67.0°$ C). Its solution in water, hydrobromic acid, is a strong acid. The principal salts of hydrobromic acid are sodium bromide, NaBr, and potassium bromide, KBr, which are used in medicine, and silver bromide, AgBr, which, like silver chloride, AgCl, and silver iodide, AgI, is used in making photographic emulsions.

Iodine. The element iodine (from Greek *iodes*, violet) occurs as iodide ion, I^-, in very small quantities in sea water, and, as **sodium iodate,** $NaIO_3$, in deposits of Chile saltpeter. It is made commercially from sodium iodate obtained from saltpeter, and also from kelp, which concentrates it from the sea water, and from oil-well brines.

The free element is an almost black crystalline solid with a slightly metallic luster. On gentle warming it gives a beautiful blue-violet vapor. Its solutions in chloroform, carbon tetrachloride, and carbon disulfide are also blue-violet in color, indicating that the molecules I_2 in these solutions closely resemble the gas molecules. The solutions of iodine in water containing potassium iodide and in alcohol (tincture of iodine)

are brown; this change in color suggests that the iodine molecules have undergone chemical reaction in these solutions. The brown compound KI_3, potassium triiodide, is present in the first solution, and a compound with alcohol in the second.

Hydrogen iodide, HI, is a colorless gas (m.p. $-50.8°$ C, b.p. $-35.3°$ C), whose solution in water, called hydriodic acid, is a strong acid.

Periodicity and Atomic Number. The value of the periodic table is clearly illustrated by the halogens. All four of the elementary substances form diatomic molecules X_2; their hydrogen compounds all have the formula HX, and their sodium salts the formula NaX. The free elements are all oxidizing agents, and their oxidizing power decreases regularly in the order F_2, Cl_2, Br_2, I_2.

The color of the free elements becomes increasingly deeper, from pale yellow to nearly black, with increase in atomic number. Some of the salts also show a trend in color; for example, from AgF and AgCl, colorless, to AgBr, pale yellow, and AgI, yellow.

In general the weak intermolecular forces that hold molecules together in liquids and crystals increase rapidly in magnitude with increase in atomic number of the atoms in the molecules. This is shown for example by the trend in melting points and boiling points of the noble gases, Table 5-2. It causes the physical state of the free halogens to vary, from a difficulty condensable gas (fluorine), through an easily condensable gas (chlorine), and a liquid (bromine), to a solid (iodine). The melting points of the halogens show nearly regular increments of about $100°$ C from each period to the next, and the boiling points show similar increments.

In your study of descriptive chemistry you may find it valuable often to compare the properties of substances with the positions of their component elements in the periodic table, in the way illustrated above.

Illustrative Exercises

13-4.   Write the equation for the reaction of methane with an excess of fluorine. What are the oxidation numbers of carbon, hydrogen, and oxygen in the reactants and the products?

13-5.   Write the electronic structure of silicon tetrafluoride.

13-6.   Can you explain by the consideration of electronegativities why hydrofluoric acid attacks glass, such as silica glass, SiO_2, whereas hydrochloric acid does not? (Compare the stability of the Si—F bond with that of the Si—Cl bond.)

13-7.   Assuming asbestos to have the formula $Ca_2Mg_5Si_8O_{24}H_2$, list the products that might be obtained by its reaction with an excess of fluorine. Write the equation for the reaction.

13-8.   How many grams of salt and how many grams of sulfuric acid (pure H_2SO_4) would be needed to prepare 22.4 l (at standard conditions) of hydrogen chloride, by the reaction given above in the discussion of hydrogen chloride?

13–3. The Preparation of the Elementary Halogens

The original method of preparing **fluorine** was the electrolysis of a solution of potassium fluoride, KF, in liquid hydrogen fluoride, HF, using as the material of the containing vessel an alloy of platinum and
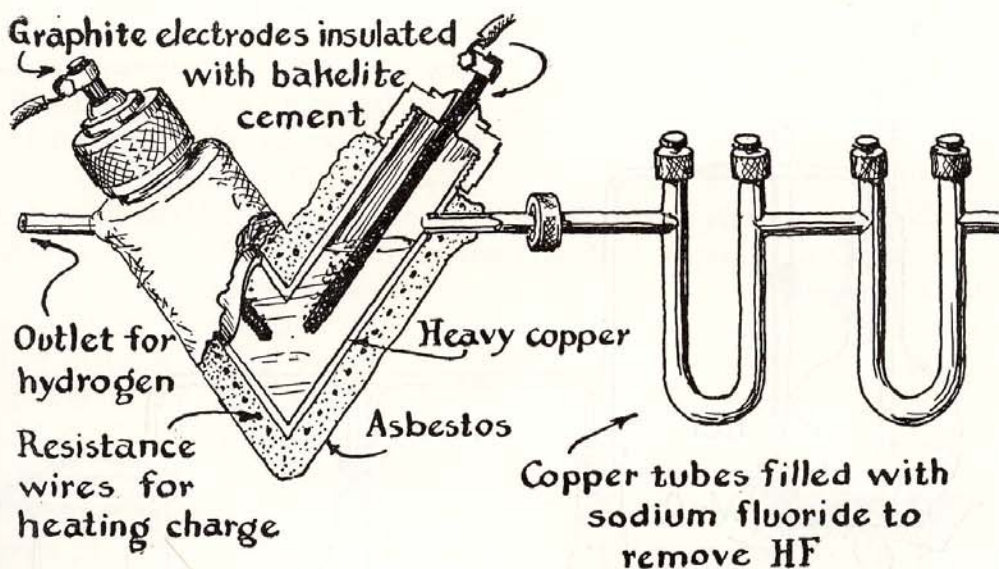
Graphite electrodes insulated with bakelite cement

Outlet for hydrogen

Resistance wires for heating charge

Heavy copper

Asbestos

Copper tubes filled with sodium fluoride to remove HF

FIGURE 13-1   *Apparatus used for preparing fluorine by electrolysis of potassium hydrogen fluoride.*

iridium. It has since been learned that copper can be used for this purpose. The copper is attacked by the fluorine, forming, however, a surface layer of copper fluoride which protects the tube from further corrosion.

The modern method of preparing fluorine in the laboratory is illustrated in Figure 13-1. The container is filled with perfectly dry potassium hydrogen fluoride, KHF_2, which is melted by passing an electric current through the resistance wires surrounding the copper tube. A direct potential is then applied between the two graphite electrodes, causing the liberation of hydrogen at the cathode, on the left, and fluorine at the anode. Hydrogen fluoride is removed from the fluorine gas by passage through a U-tube filled with sodium fluoride, which combines with hydrogen fluoride to form the crystalline substance sodium hydrogen fluoride, $NaHF_2$.

Chlorine is conveniently made in the laboratory by the oxidation of hydrochloric acid with either manganese dioxide or potassium permanganate. Manganese dioxide is placed in a flask, as shown in Figure 13-2, and concentrated hydrochloric acid is added through a funnel. Chlorine is evolved according to the equation

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2 \uparrow$$

This equation represents the over-all reaction, which in fact takes place in two stages. At room temperature manganese is reduced from the quadripositive state to the terpositive state, with liberation of a corresponding amount of chlorine:
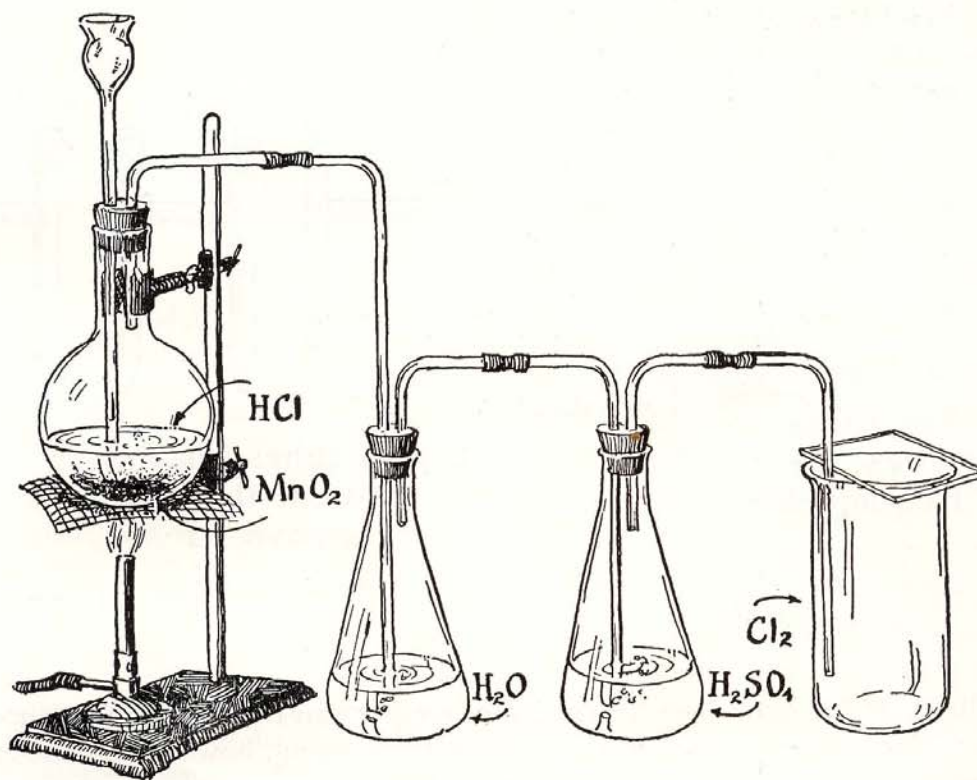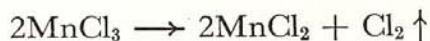
$$2MnO_2 + 8HCl \longrightarrow 2MnCl_3 + 4H_2O + Cl_2 \uparrow$$

FIGURE 13-2   *The preparation of chlorine by the reaction of hydrochloric acid and manganese dioxide.*

When the mixture is heated a further reaction takes place, with reduction of manganese to the bipositive state:

$$2MnCl_3 \longrightarrow 2MnCl_2 + Cl_2 \uparrow$$

The liberated chlorine is bubbled through a small amount of water, to remove hydrogen chloride, and then through concentrated sulfuric acid, to remove water vapor. The gas is over twice as heavy as air (molecular weight 71, as compared with average molecular weight 29 for air) and can accordingly be collected by upward displacement of air.

The preparation of chlorine by use of potassium permanganate is carried out in the same way, except that it is not necessary to heat the reaction mixture. Crystals of potassium permanganate are placed in a flask of an apparatus similar to that of Figure 13-2, except that the funnel for introducing the hydrochloric acid is provided with a stopcock. Hydrochloric acid is then permitted to drip into the funnel, the stopcock being closed after the reaction has begun to take place at a sufficiently rapid rate. The equation for the over-all reaction is

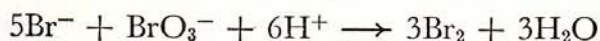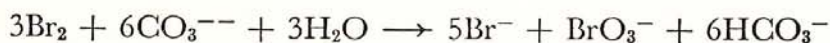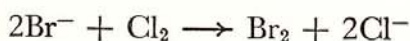$$2KMnO_4 + 16HCl \longrightarrow 2MnCl_2 + 2KCl + 8H_2O + 5Cl_2$$

Chlorine can also be prepared, with such an apparatus, by allowing concentrated hydrochloric acid to react with bleaching powder.

Chlorine for commercial use is made by electrolysis of molten sodium chloride, as described in Chapter 10, or of brine.

Bromine can be prepared in the laboratory by the action of sulfuric acid on a mixture of sodium bromide and manganese dioxide, in the apparatus shown in Figure 13-2. Until recently most of the bromine used commercially was made in this way, from sodium bromide and potassium bromide mined from the Stassfurt deposits in Germany, or from brines pumped from wells in the eastern and central United States. During the past twenty-five years there has occurred a very great increase in the amount of bromine manufactured, until at present over 10,000 tons a year is being made.

Most of the bromine produced is converted into ethylene dibromide, $C_2H_4Br_2$, which is an important constituent of "ethyl gas," together with tetraethyl lead, $(C_2H_5)_4Pb$. Tetraethyl lead has valuable anti-knock properties, but its continued use would cause damage to a motor through the deposition of metallic lead, unless some way were found to eliminate this deposit. The ethylene dibromide that is added to the gasoline provides bromine on combustion, which combines with the lead, permitting its elimination as lead bromide, $PbBr_2$.

The great amount of bromine required for this purpose and other uses at the present time is obtained by extraction of the element from sea water, which contains about 70 parts of bromine, as bromide ion, per million of water. The process of extraction involves four steps: oxidation with chlorine to convert the bromide ion to free bromine, removal of the bromine from the solution by bubbling a stream of air through it, absorption of the bromine from the air by bubbling through a solution of sodium carbonate, and treatment of the solution with sulfuric acid to liberate the elementary bromine. The equations for the successive reactions are

$$2Br^- + Cl_2 \longrightarrow Br_2 + 2Cl^-$$

$$3Br_2 + 6CO_3^{--} + 3H_2O \longrightarrow 5Br^- + BrO_3^- + 6HCO_3^-$$

$$5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

The acidified reaction mixture is boiled, and the bromine is condensed from the vapor.

Iodine is conveniently made in the laboratory from sodium iodide, by the method described above for making bromine from a bromide.

Illustrative Exercises

13-9.   Write the electrode reactions and the over-all reaction for the preparation of fluorine by electrolysis of potassium hydrogen fluoride.

13-10.   How many liters of fluorine at 0° C and 1 atm would be produced by a current of 10 amperes in 9650 seconds?

13-11.   Write the equation for production of chlorine by reaction of permanganate ion, MnO_4^-, with hydrogen ion and chloride ion, in aqueous solution. Manganese(II) ion, Mn^{++}, is also a product.

13-12.   Write the equations for the combustion of tetraethyl lead to form carbon dioxide, water, and lead, the combustion of ethylene dibromide to form carbon dioxide, water, and bromine, and the reaction of lead and bromine to form lead(II) bromide. These reactions take place in a gasoline engine using ethyl gasoline.

13-13.   How many grams of ethylene dibromide would you calculate to be needed in ethyl gasoline per gram of tetraethyl lead?

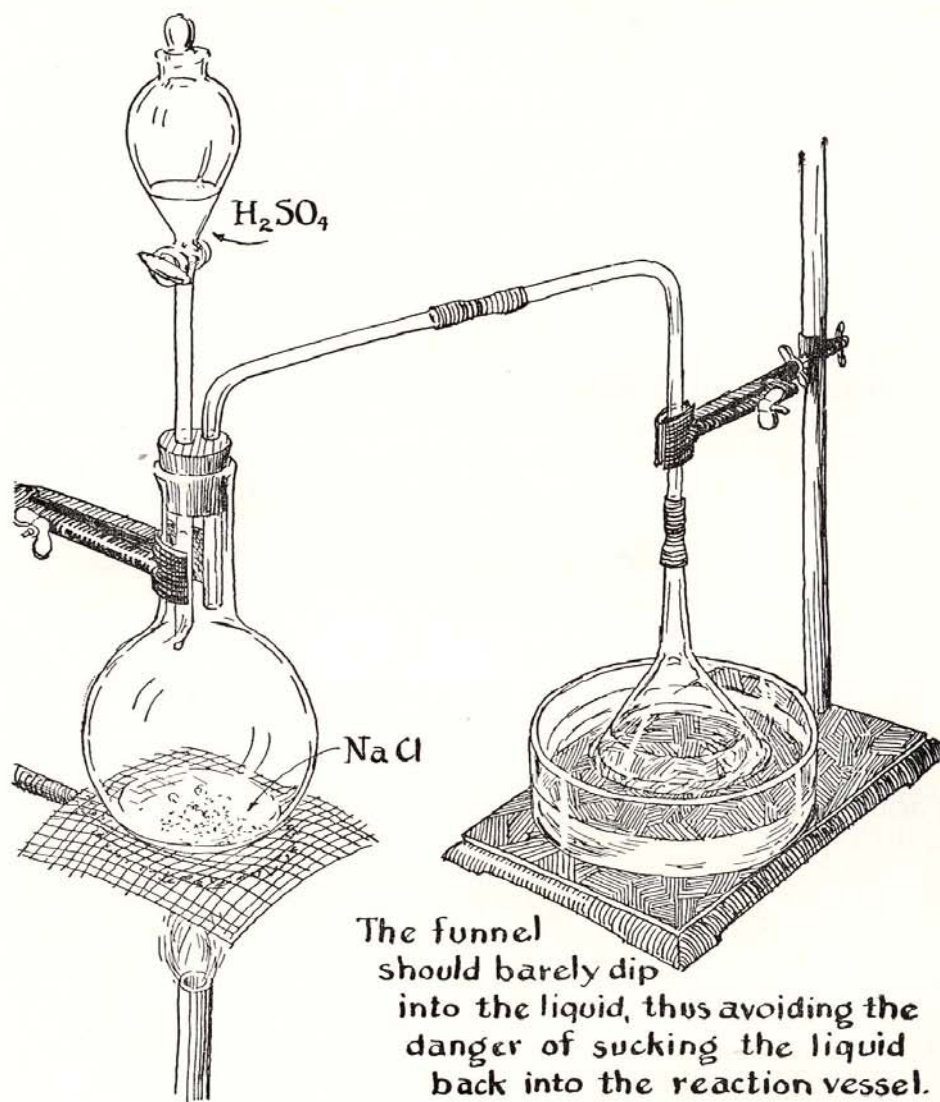13-14.   Write an equation for the reaction of sulfuric acid, manganese dioxide, and sodium iodide to prepare iodine.

The funnel should barely dip into the liquid, thus avoiding the danger of sucking the liquid back into the reaction vessel.

FIGURE 13-3   *Apparatus for the preparation of hydrogen chloride and hydrochloric acid.*

13–4. *The Preparation of the Hydrogen Halides*

It was mentioned in Section 13–2 that **hydrogen fluoride**, HF, is made by treating fluorite with sulfuric acid. This reaction is usually carried out in a lead dish or a platinum dish; in the commercial manufacture of hydrofluoric acid it is carried out in an iron pot, which is connected with a series of lead boxes containing water, in which the hydrogen fluoride dissolves to form aqueous hydrofluoric acid. Pure, anhydrous hydrogen fluoride is best made by heating potassium hydrogen fluoride, KHF_2. This salt can be easily crystallized from a potassium fluoride solution to which hydrofluoric acid has been added.

Hydrogen chloride is made by the reaction of sodium chloride and
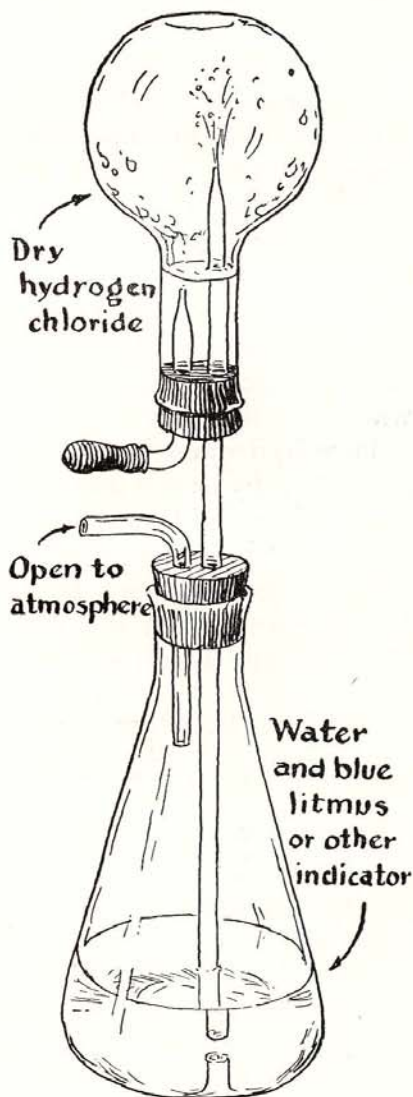

FIGURE 13-4

The hydrogen chloride fountain; the same experiment can be carried out with ammonia instead of hydrogen chloride.

sulfuric acid. The apparatus shown in Figure 13-3 may be used for this purpose. The sulfuric acid is dropped onto sodium chloride as shown; since concentrated sulfuric acid absorbs water, the gas that is evolved is dry, and it may be collected directly in bottles by upward displacement of air. In case that a solution of hydrochloric acid is to be prepared, care must be taken in leading the gas into water, because its great solubility in water might cause the solution to be sucked back into the reaction vessel. A safety device designed to prevent this is shown in the figure; it consists of an inverted funnel, through which the gas is led into the water. The mouth of the funnel is dipped only a small distance under the surface of the water, in such a way that if the solution begins to be sucked back the water level is lowered enough to permit air to enter. The reaction between cold sulfuric acid and sodium chloride leads to the formation of sodium hydrogen sulfate, $NaHSO_4$.

An amusing experiment demonstrating the great solubility of hydrogen chloride in water can be carried out. This experiment, called the hydrogen chloride fountain, makes use of the apparatus shown in Figure 13-4. A dry flask filled with hydrogen chloride and equipped with a 2-hole stopper with a dropper with rubber bulb in one hole is placed over a glass tube, which dips beneath the surface of water in a lower flask and is drawn out to a nozzle at its upper end. The reaction is begun by pressing the small rubber bulb, so as to introduce a few drops of water into the upper flask. The immediate solution of the hydrogen chloride in this water causes a decrease in pressure, which sucks water into the upper flask from the lower flask in a rapid stream.

Pure **hydrogen bromide** cannot be prepared by the same methods as used for hydrogen fluoride and hydrogen chloride, involving displacement of the acid from one of its salts by sulfuric acid. Sulfuric acid even at room temperature is a sufficiently strong oxidizing agent to oxidize some of the hydrogen bromide, causing it to be contaminated with bromine and sulfur dioxide. The reactions that take place when the effort is made to prepare hydrogen bromide in this way are the following:

$$KBr + H_2SO_4 \longrightarrow KHSO_4 + HBr \uparrow$$

$$2HBr + H_2SO_4 \longrightarrow 2H_2O + SO_2 \uparrow + Br_2 \uparrow$$
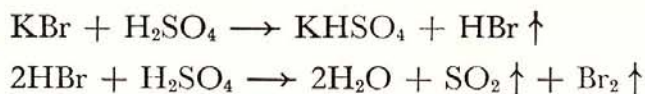
The preparation can be carried out with phosphoric acid in place of sulfuric acid, but it is customary instead to prepare hydrogen bromide in the laboratory by the hydrolysis of phosphorus tribromide, PBr_3. The reaction can be carried out by mixing red phosphorus with wet sand, placing the mixture in a flask equipped with a dropping funnel and an outlet tube, and allowing the bromine to drip onto the red phosphorus. Phosphorus and bromine immediately react, to form phosphorus tribromide, which at once hydrolyzes with the water present:

$$2P + 3Br_2 \longrightarrow 2PBr_3$$
$$PBr_3 + 3H_2O \longrightarrow P(OH)_3 + 3HBr \uparrow$$
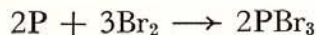
The gas that is evolved is passed through a U-tube containing glass beads mixed with red phosphorus, which combines with any bromine that may be carried along with it. The hydrogen bromide may be collected by upward displacement of air, or may be absorbed in water, with use of a safety device such as shown in Figure 13-3, to form hydrobromic acid.

Hydrogen bromide can also be made by direct combination of the elements. If a stream of hydrogen is bubbled through bromine contained in a flask heated on a water bath to 38° C, the gas mixture that is produced contains hydrogen and bromine in approximately equimolecular proportions. This gas may be passed over platinized silicic acid, which acts as a catalyst, causing the combination of hydrogen and bromine:

$$H_2 + Br_2 \longrightarrow 2HBr$$
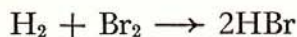
The reaction can also be made to take place in a heated tube filled with pieces of porous clay plate.

Hydrogen bromide can also be made by the reduction of bromine with hydrogen sulfide:

$$H_2S + Br_2 \longrightarrow 2HBr + S$$
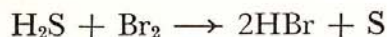
The gas that is produced can be purified of bromine by passing over red phosphorus, as described in the first method.

Hydrogen iodide, which is still more easily oxidized than hydrogen bromide, can be prepared by similar methods. The customary method of preparation involves the reaction of water, iodine, and red phosphorus. Iodine and red phosphorus are mixed and placed in a flask, to which water is admitted from a dropping funnel. The reaction involved is

$$2P + 3I_2 + 6H_2O \longrightarrow 2P(OH)_3 + 6HI \uparrow$$
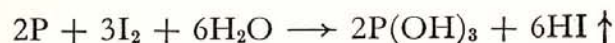
Illustrative Exercises

13-15. Hydrogen chloride can be made by heating a mixture of sodium hydrogen sulfate and sodium chloride. Write the equation for the reaction.

13-16. Why cannot pure hydrogen iodide be made by use of sulfuric acid and sodium iodide? Write equations for two reactions that might take place if these substances were mixed.

13-17. It is stated above that when a stream of hydrogen is bubbled through bromine at 38° C the gas mixture produced is equimolecular in H_2 and Br_2. What is the vapor pressure of liquid bromine at 38° C? (Ans. About 380 mm Hg)

13–5. *The Oxygen Acids and Oxides of Chlorine*

The oxygen acids of chlorine and their anions have the following formulas and names:

$HClO_4$, perchloric acid ClO_4^-, perchlorate ion
$HClO_3$, chloric acid ClO_3^-, chlorate ion
$HClO_2$, chlorous acid ClO_2^-, chlorite ion
$HClO$, hypochlorous acid ClO^-, hypochlorite ion

The electronic structures of the four anions are shown in Figure 13-5.

In the following sections these acids and their salts, and also the oxides of chlorine, are discussed in the order of increasing oxidation number of the halogen.

Hypochlorous Acid and the Hypochlorites. Hypochlorous acid, $HClO$, and most of its salts are known only in aqueous solution; they decompose when the solution is concentrated. A mixture of chloride ion and hypochlorite ion is formed when chlorine is bubbled through a solution of sodium hydroxide:

$$Cl_2 + 2OH^- \longrightarrow Cl^- + ClO^- + H_2O$$

A solution of **sodium hypochlorite**, $NaClO$, made in this way or by electrolysis of sodium chloride solution is a popular household sterilizing and bleaching agent. The hypochlorite ion is an active oxidizing agent, and its oxidizing power is the basis of its sterilizing and bleaching action.
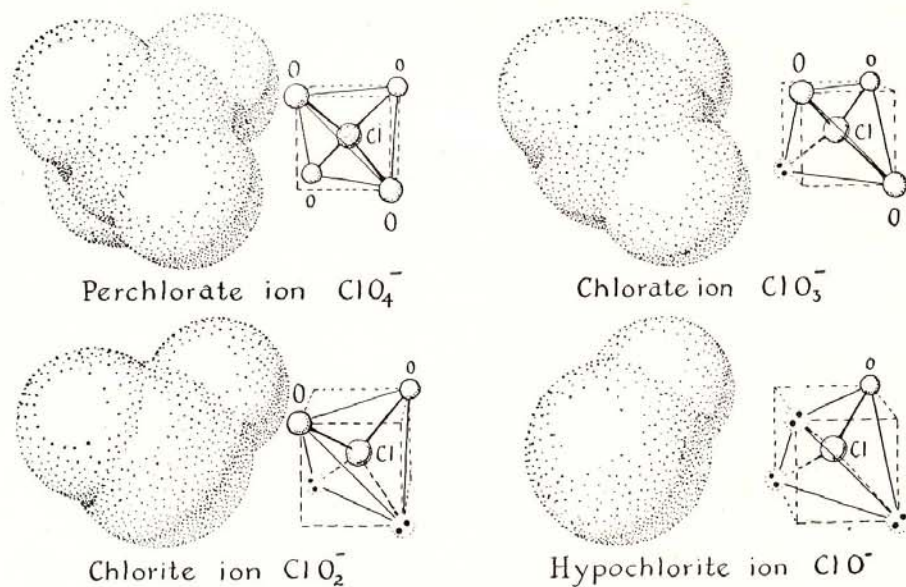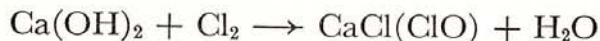

Perchlorate ion ClO_4^- Chlorate ion ClO_3^-

Chlorite ion ClO_2^- Hypochlorite ion ClO^-

FIGURE 13-5   *The structure of ions of the four oxygen acids of chlorine.*

Bleaching powder is a compound obtained by passing chlorine over calcium hydroxide:

$$Ca(OH)_2 + Cl_2 \longrightarrow CaCl(ClO) + H_2O$$

The formula $CaCl(ClO)$, which approximates the composition of commercial bleaching powder, indicates it to be a calcium chloride-hypochlorite, containing the two anions Cl^- and ClO^-. Bleaching powder is a white, finely-powdered substance which usually smells of chlorine, because of its decomposition by water vapor in the air. It is often called by the incorrect name "chloride of lime." It is used as a household bleaching and sterilizing agent; in its former industrial use, for bleaching paper pulp and textile fabrics, it has been largely displaced by liquid chlorine. Pure **calcium hypochlorite,** $Ca(ClO)_2$, is also manufactured and used as a bleaching agent.

Hypochlorous acid is a weak acid. The solution obtained by adding another acid, such as sulfuric acid, to a solution of a hypochlorite contains molecules $HClO$, and very few hypochlorite ions ClO^-:

$$ClO^- + H^+ \longrightarrow HClO$$
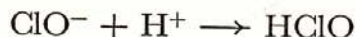
Dichlorine monoxide, Cl_2O, is a yellow gas obtained by gently heating hypochlorous acid in a partially evacuated system (that is, under reduced pressure):

$$2HClO \longrightarrow H_2O + Cl_2O \uparrow$$
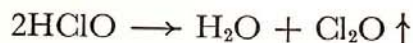
or by passing chlorine over mercuric oxide:

$$2Cl_2 + HgO \longrightarrow HgCl_2 + Cl_2O \uparrow$$
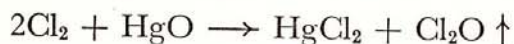
The gas condenses to a liquid at about 4° C. It is the anhydride of hypochlorous acid: that is, it reacts with water to give hypochlorous acid:

$$Cl_2O + H_2O \longrightarrow 2HClO$$
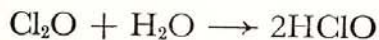
The electronic structure of chlorine monoxide is $: \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} \!\!-\!\! \overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}} :$, in which with a $: \overset{\cdot\cdot}{Cl} :$ above, in which

chlorine and oxygen have their normal covalences of 1 and 2, respectively.

Chlorous Acid and the Chlorites.   When chlorine dioxide, ClO_2, is passed into a solution of sodium hydroxide or other alkali a chlorite ion and a chlorate ion are formed:

$$2ClO_2 + 2OH^- \longrightarrow ClO_2^- + ClO_3^- + H_2O$$

This is an auto-oxidation-reduction reaction, the chlorine with oxidation number +4 in chlorine dioxide being reduced and oxidized simultaneously to oxidation numbers +3 and +5. Pure sodium chlorite, $NaClO_2$, can be made by passing chlorine dioxide into a solution of sodium peroxide:

$$2ClO_2 + Na_2O_2 \longrightarrow 2Na^+ + 2ClO_2^- + O_2$$
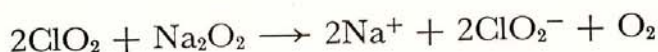
In this reaction the peroxide oxygen serves as a reducing agent, decreasing the oxidation number of chlorine from +4 to +3.

Sodium chlorite is an active bleaching agent, used in the manufacture of textile fabrics.

Chlorine Dioxide. Chlorine dioxide, ClO_2, is the only compound of quadripositive chlorine. It is a reddish-yellow gas, which is very explosive, decomposing readily to chlorine and oxygen. The violence of this decomposition makes it very dangerous to add sulfuric acid or any other strong acid to a chlorate or to any dry mixture containing a chlorate.

Chlorine dioxide can be made by carefully adding sulfuric acid to potassium chlorate, $KClO_3$. It would be expected that this mixture would react to produce chloric acid, $HClO_3$, and then, because of the dehydrating power of sulfuric acid, to produce the anhydride of chloric acid, Cl_2O_5:

$$KClO_3 + H_2SO_4 \longrightarrow KHSO_4 + HClO_3$$

$$2HClO_3 \longrightarrow H_2O + Cl_2O_5$$
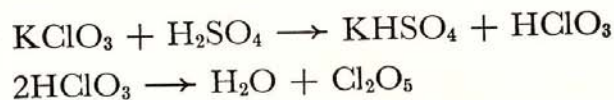
However, dichlorine pentoxide, Cl_2O_5, is very unstable—its existence has never been verified. If it is formed at all, it decomposes at once to give chlorine dioxide and oxygen:

$$2Cl_2O_5 \longrightarrow 4ClO_2 + O_2$$
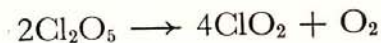
The over-all reaction may be written as

$$4KClO_3 + 4H_2SO_4 \longrightarrow 4KHSO_4 + 4ClO_2\uparrow + O_2\uparrow + 2H_2O$$

Chlorine dioxide is an **odd molecule;** that is, a molecule containing an odd number of electrons. It was pointed out by G. N. Lewis in 1916 that odd molecules (other than those containing transition elements) are rare, and that they are usually colored and are always paramagnetic (attracted by a magnet). Every electronic structure that can be written for chlorine dioxide contains one unpaired electron. This unpaired electron presumably resonates among the three atoms, the electronic structure of the molecule being a resonance hybrid:
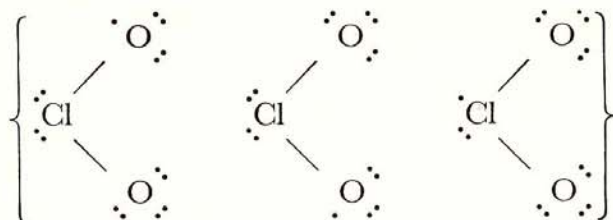
It was mentioned in the preceding section that when chlorine dioxide is dissolved in an alkaline solution chlorate ion and chlorite ion are formed.

Chloric Acid and Its Salts.   Chloric acid, $HClO_3$, is an unstable acid which, like its salts, is a strong oxidizing agent. The most important salt of chloric acid is **potassium chlorate, $KClO_3$**, which is made by passing an excess of chlorine through a hot solution of potassium hydroxide or by heating a solution containing hypochlorite ion and potassium ion:

$$3ClO^- \longrightarrow ClO_3^- + 2Cl^-$$

The potassium chlorate can be separated from the potassium chloride formed in this reaction by crystallization, its solubility at low temperatures being much less than that of the chloride (3 g and 28 g, respectively, per 100 g of water at 0° C). A cheaper way of making potassium chlorate is to electrolyze a solution of potassium chloride, using inert electrodes and keeping the solution mixed. The electrode reactions are

Cathode reaction: $2e^- + 2H_2O \longrightarrow 2OH^- + H_2 \uparrow$

Anode reaction: $Cl^- + 3H_2O \longrightarrow ClO_3^- + 6H^+ + 6e^-$
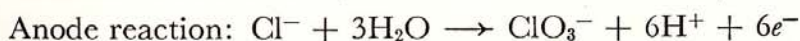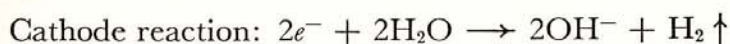
In the stirred solution the hydroxide ions and the hydrogen ions are brought into contact with one another, and combine to form water. The over-all reaction is

$$Cl^- + 3H_2O \xrightarrow{\text{electr.}} ClO_3^- + 3H_2 \uparrow$$
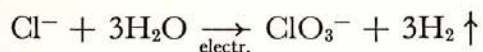
Potassium chlorate is a white crystalline substance, which is used as the oxidizing agent in matches and fireworks, and in the manufacture of dyes.

A solution of the similar salt **sodium chlorate, $NaClO_3$**, is used as a weed-killer. Potassium chlorate would be as good as sodium chlorate for this purpose; however, sodium salts are cheaper than potassium salts, and for this reason they are often used when only the anion is important. Sometimes the sodium salts have unsatisfactory properties, such as *deliquescence* (attraction of water from the air to form a solution),

which make the potassium salts preferable for some uses, even though more expensive.

All of the chlorates form sensitive explosive mixtures when mixed with reducing agents; **great care must be taken in handling them.** The use of sodium chlorate as a weed-killer is attended with danger, because combustible material such as wood or clothing that has become saturated with the chlorate solution will ignite by friction after it has dried. Also *it is very dangerous to grind a chlorate with sulfur, charcoal, or other reducing agent.*

Perchloric Acid and the Perchlorates. Potassium **perchlorate,** $KClO_4$, is made by heating potassium chlorate just to its melting point:

$$4KClO_3 \longrightarrow 3KClO_4 + KCl$$

At this temperature very little decomposition with evolution of oxygen occurs in the absence of a catalyst. Potassium perchlorate may also be made by long-continued electrolysis of a solution of potassium chloride, potassium hypochlorite, or potassium chlorate.

Potassium perchlorate and other perchlorates are oxidizing agents, somewhat less vigorous and less dangerous than the chlorates. Potassium perchlorate is used in explosives, such as the propellent powder of the bazooka and other rockets. This powder is a mixture of potassium perchlorate and carbon together with a binder; the equation for the principal reaction accompanying its burning is

$$KClO_4 + 4C \longrightarrow KCl + 4CO$$

Anhydrous **magnesium perchlorate,** $Mg(ClO_4)_2$, and **barium perchlorate,** $Ba(ClO_4)_2$, are used as drying agents (*desiccants*). These salts have a very strong attraction for water. Nearly all of the perchlorates are highly soluble in water; potassium perchlorate is exceptional for its low solubility, 0.75 g/100 g at 0° C.

Sodium perchlorate, $NaClO_4$, made by the electrolytic method, is used as a weed-killer; it is safer than sodium chlorate. In general the mixtures of perchlorates with oxidizable materials are less dangerous than the corresponding mixtures of chlorates.

Perchloric acid, $HClO_4 \cdot H_2O$, is a colorless liquid made by distilling, under reduced pressure, a solution of a perchlorate to which sulfuric acid has been added. The perchloric acid distills as the monohydrate, and on cooling it forms crystals of the monohydrate. These crystals are isomorphous with ammonium perchlorate, NH_4ClO_4, and the substance is presumably hydronium perchlorate, $(H_3O)^+(ClO_4)^-$.

Dichlorine heptoxide, Cl_2O_7, is the anhydride of perchloric acid. It can be made by heating perchloric acid with P_2O_5, a strong dehydrating agent:

$$2HClO_4 \cdot H_2O + P_2O_5 \longrightarrow 2H_3PO_4 + Cl_2O_7$$
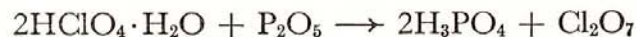
It is a colorless, oily liquid having a boiling point of $80°$ C. It is the most stable oxide of chlorine, but is exploded by heat or shock.

Illustrative Exercises

13-18.   When chlorine is passed into a solution of potassium hydroxide, chloride ions and hypochlorite ions are formed. If the solution is heated the hypochlorite ions undergo auto-oxidation to chlorate ions and chloride ions. Write equations for the two reactions.

13-19.   What reaction takes place when Cl_2O is added to water? When ClO_2 is added to water? When Cl_2O_7 is added to water? Would you consider each of these oxides to be an acid anhydride?

13–6. *The Oxygen Acids and Oxides of Bromine*

Bromine forms only two stable oxygen acids—hypobromous acid and bromic acid—and their salts:

HBrO, hypobromous acid   KBrO, potassium hypobromite
$HBrO_3$, bromic acid $KBrO_3$, potassium bromate

Their preparation and properties are similar to those of the corresponding compounds of chlorine. They are somewhat weaker oxidizing agents than their chlorine analogs.

The bromite ion, BrO_2^-, has been reported to exist in solution. However, no effort to prepare perbromic acid or any perbromate has succeeded.

Three very unstable oxides of bromine, Br_2O, BrO_2, and Br_3O_8, have been described. The structure of Br_3O_8 is not known.

None of the oxygen compounds of bromine has found important practical use.

13–7. *The Oxygen Acids and Oxides of Iodine*

Iodine reacts with hydroxide ion in cold alkaline solution to form the **hypoiodite ion, IO^-**, and iodide ion:

$$I_2 + 2OH^- \longrightarrow IO^- + I^- + H_2O$$

On warming the solution it reacts further to form **iodate ion, IO_3^-**:

$$3IO^- \longrightarrow IO_3^- + 2I^-$$

The salts of hypoiodous acid and iodic acid may be made in these ways. **Iodic acid** itself, HIO_3, is usually made by oxidizing iodine with concentrated nitric acid:
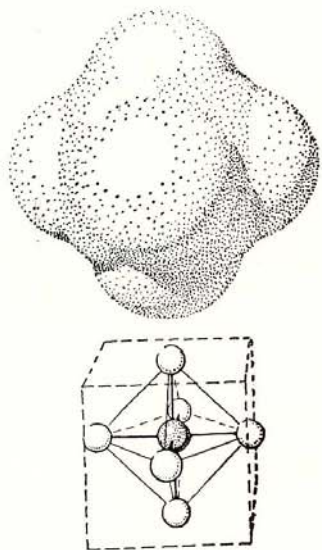
$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 \uparrow + 4H_2O$$

FIGURE 13-6

The periodate ion, IO_6^{5-}.

Iodic acid is a white solid, which is only very slightly soluble in concentrated nitric acid; it accordingly separates out during the course of the reaction. Its principal salts, **potassium iodate**, KIO_3, and **sodium iodate**, $NaIO_3$, are white crystalline solids.

Periodic acid has the normal formula H_5IO_6, with an octahedral arrangement of the oxygen atoms around the iodine atom, as shown in Figure 13-6. This difference in composition from its analog perchloric acid, $HClO_4$, results from the large size of the iodine atom, which permits this atom to coordinate six oxygen atoms about itself, instead of four. The ligancy of iodine in periodic acid is hence 6.

There exists a series of periodates corresponding to the formula H_5IO_6 for periodic acid, and also a series corresponding to HIO_4. Salts of the first series are **dipotassium trihydrogen periodate**, $K_2H_3IO_6$, **silver periodate**, Ag_5IO_6, etc. **Sodium periodate**, $NaIO_4$, a salt of the second series, occurs in small amounts in crude Chile saltpeter. A solution of sodium periodate usually crystallizes as $Na_2H_3IO_6$, a salt of the first series.

The two forms of periodic acid, H_5IO_6 and HIO_4 (the latter being unstable, but forming stable salts), represent the same oxidation state of iodine, $+7$. The equilibrium between the two forms is a hydration reaction:

$$HIO_4 + 2H_2O \rightleftarrows H_5IO_6$$
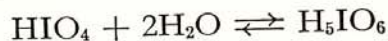
The Oxides of Iodine. **Iodine pentoxide**, I_2O_5, is obtained as a white powder by gently heating either iodic acid or periodic acid:

$$2HIO_3 \longrightarrow I_2O_5 + H_2O \uparrow$$

$$2H_5IO_6 \longrightarrow I_2O_5 + 5H_2O \uparrow + O_2 \uparrow$$
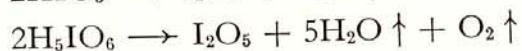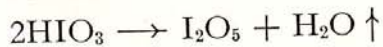
The anhydride of periodic acid, I_2O_7, seems not to be stable.

The lower oxide of iodine, IO_2, can be made by treating an iodate with concentrated sulfuric acid and then adding water. This oxide is a yellow solid. The magnetic properties of the substance show that its formula is not I_2O_4; the substance is paramagnetic, which shows that it has an odd number of electrons in the molecule.

13–8. *The Oxidizing Strength of the Oxygen Compounds of the Halogens*

Elementary fluorine, F_2, is able to oxidize the halide ions of its congeners to the free halogens, by reactions such as

$$F_2 + 2Cl^- \longrightarrow 2F^- + Cl_2$$
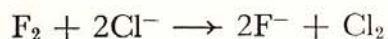
Fluorine is more electronegative than the other elements, and it accordingly is able to take electrons away from the anions of these elements. Similarly chlorine is able to oxidize both bromide ion and iodide ion, and bromine is able to oxidize iodide ion:

$$Cl_2 + 2Br^- \longrightarrow 2Cl^- + Br_2$$
$$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$$
$$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$$
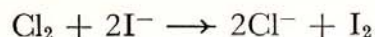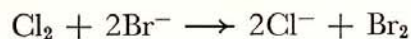
The order of strength as an oxidizing agent for the elementary halogens is accordingly $F_2 > Cl_2 > Br_2 > I_2$.

At first sight there seems to be an anomaly in the reactions involving the free halogens and their oxygen compounds. Thus, although chlorine is able to liberate iodine from iodide ion, iodine is able to liberate chlorine from chlorate ion, according to the reaction

$$I_2 + 2ClO_3^- \longrightarrow 2IO_3^- + Cl_2$$

In this reaction, however, it is to be noted that elementary iodine is acting as a reducing agent, rather than as an oxidizing agent. During the course of the reaction the oxidation number of iodine is increased, from 0 to +5, and that of chlorine is decreased, from +5 to 0. The direction in which the reaction takes place predominantly is accordingly that which would be predicted by the electronegativity scale; iodine, the heavier halogen and less electronegative element, tends to have a high positive oxidation number, and chlorine tends to have a low oxidation number. (Remember that in this case, as in nearly all chemical reactions, we may be dealing with chemical equilibrium. The foregoing statement is to be interpreted as meaning that at equilibrium there are present in the system larger amounts of iodate ion and free chlorine than of chlorate ion and free iodine.)

Chlorate ion also has the power of oxidizing free bromine to bromate ion, and bromate ion has the power of oxidizing free iodine to iodate ion:

$$Br_2 + 2ClO_3^- \longrightarrow 2BrO_3^- + Cl_2$$

$$I_2 + 2BrO_3^- \longrightarrow 2IO_3^- + Br_2$$
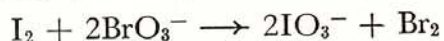
Chlorate ion is hence a stronger oxidizing agent than bromate ion, which in turn is a stronger oxidizing agent than iodate ion; conversely, iodine is a stronger reducing agent than bromine, which is itself a stronger reducing agent than chlorine. All of these relations correspond to the electronegativity scale. The oxidizing and reducing strengths of hypochlorite ion, hypobromite ion, and hypoiodite ion also correspond to expectation; hypochlorite ion is the strongest oxidizing agent and the weakest reducing agent of the three.

Illustrative Exercises

13-20. Would you predict that iodine would react with chloride ion? With chlorate ion?

13-21. Write an equation for the reaction of bromine with a solution of potassium hydroxide.

13-22. Would you expect iodine to be a stronger or a weaker disinfectant than chlorine? Why?

13-23. Bromine forms only two oxygen acids, HBrO and $HBrO_3$. Write an equation for the reaction that you would expect to occur when the oxide BrO_2 is added to water.

13–9. Compounds of Halogens with Non-Metals and Metalloids

The halogens form covalent compounds with most of the non-metallic elements (including each other) and the metalloids. These compounds are usually molecular substances, with the relatively low melting points and boiling points characteristic of substances with small forces of intermolecular attraction.

An example of a compound involving a covalent bond between a halogen and a non-metal is chloroform, $CHCl_3$ (Chapter 7). In this molecule, the structure of which is shown in Figure 13-7, the carbon atom is attached by single covalent bonds to one hydrogen atom and three chlorine atoms. Chloroform is a colorless liquid, with a characteristic sweetish odor. Its boiling point is 61° C and its density is 1.498 g/ml. Chloroform is only slightly soluble in water, but it dissolves readily in alcohol, ether, and carbon tetrachloride.

FIGURE 13-7

The chloroform molecule, CHCl₃.
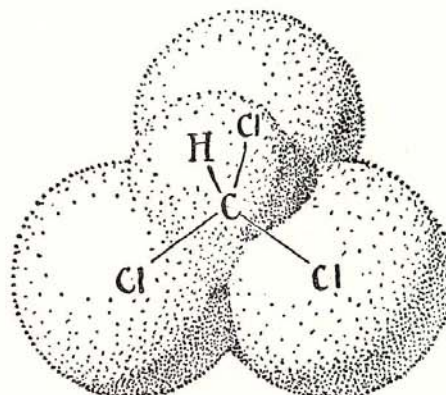
The melting points and boiling points of some binary covalent chlorides are the following:

	CCl_4	NCl_3	Cl_2O	ClF
m.p.	$-23°$	$-40°$	$-20°$	$-154°$ C
b.p.	$77°$	$70°$	$4°$	$-100°$

	$SiCl_4$	PCl_3	SCl_2	Cl_2
m.p.	$-70°$	$-112°$	$-78°$	$-102°$
b.p.	$60°$	$74°$	$59°$	$-34°$

	$GeCl_4$	$AsCl_3$
m.p.	$-50°$	$-18°$
b.p.	$83°$	$130°$

	$SnCl_4$	$SbCl_3$	$TeCl_2$	ICl
m.p.	$-33°$	$73°$	$209°$	$27°$
b.p.	$114°$	$223°$	$327°$	$97°$

In addition to these compounds, many compounds, such as PCl_5, ClF_3, SCl_4, etc., exist, to which a normal covalent structure with noble-gas configuration for the central atom cannot be assigned.

Many of these substances react readily with water, to form a hydride of one element and a hydroxide of the other:

$$ClF + H_2O \longrightarrow HClO + HF$$
$$PCl_3 + 3H_2O \longrightarrow P(OH)_3 + 3HCl$$
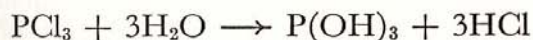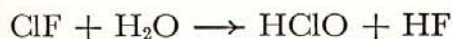
In general, in a reaction of this sort, called *hydrolysis,* the more electronegative element combines with hydrogen, and the less electronegative element combines with the hydroxide group. This rule is seen to be followed in the above examples.

Concepts, Facts, and Terms Introduced in This Chapter

The oxidation states of the halogens. Properties of the halogens and halogenides.

Methods of preparing the halogens and the hydrogen halogenides.

$HClO_4$, $HClO_3$, $HClO_2$, $HClO$, and their salts.

$HBrO_3$, $HBrO$, and their salts.

$H_5 O_6$ and its salts; salts of HIO_4.

The oxides of the halogens.

ClO_2, an odd molecule; color and paramagnetism of odd molecules.

The strength of halogen compounds as oxidizing and reducing agents in relation to electronegativity.

Compounds of halogens with non-metals and metalloids; hydrolysis.

Bleaching powder; potassium chlorate; sodium chlorate; potassium perchlorate; magnesium perchlorate and barium perchlorate.

Exercises

13-24.   What chemical reaction do you expect to take place when a solution of bleaching powder is acidified? Could this be used as a method of producing hypochlorous acid?

13-25.   What chemical reaction takes place at each electrode in the electrolytic preparation of sodium hypochlorite from sodium chloride? Would a well stirred solution become more acidic or more basic during the course of this electrolysis?

13-26.   Which is the stronger oxidizing agent, hypochlorite ion, ClO^-, or hypoiodite ion, IO^-? Which is the stronger reducing agent?

13-27.   Why is potassium chlorate rather than sodium chlorate usually used in the chemical laboratory when a chlorate is needed? Why is sodium chlorate solution, rather than potassium chlorate solution, used as a weed-killer?

13-28.   Write the equation for the formation of potassium iodate by the reaction of powdered iodine with a hot solution of potassium hydroxide.

13-29.   Under what conditions does potassium chlorate decompose to give oxygen and potassium chloride, and under what conditions does it react to form potassium perchlorate and potassium chloride?

13-30.   What is the equation for the hydrolysis of chlorine monoxide? Is there any oxidation or reduction in this chemical reaction? If so, what element changes its oxidation number?

13-31.   Write an equation for the reaction of chlorine with carbon disulfide, CS_2. The products of the reaction are carbon tetrachloride, CCl_4, and disulfur dichloride, S_2Cl_2. What do you think the structure of disulfur dichloride is?

13-32.   Phosgene, $COCl_2$, is made by mixing carbon monoxide with chlorine in the sunlight or in the presence of a catalyst. Write the equation for this reaction, assigning oxidation numbers to the elements in the reactants and the product. What do you think the electronic structure of phosgene is?

13-33.   What halogen forms no oxygen acids? Does this halogen form any compounds containing oxygen?

13-34. What are the names of the compounds $CaCl_2$, $Ca(ClO)_2$, $Ca(ClO_2)_2$, $Ca(ClO_3)_2$, $Ca(ClO_4)_2$? What is the oxidation number of chlorine in each compound?

13-35. If liquid chlorine costs 5 cents per pound, and bleaching powder approximating the formula $CaOCl_2$ costs 3 cents per pound, which is the less expensive material to use to purify the water of a swimming pool?

13-36. In a mixture of sodium iodide, sodium bromide, sodium chloride, and sodium fluoride, what oxidizing agent could be used to oxidize the iodide to free iodine without affecting any of the others? After the oxidation of the iodide, what substance could be used to oxidize only the bromide? Then only the chloride? Can the fluoride be oxidized?

13-37. How can each of the four halogens be conveniently prepared from compounds in the laboratory? Write equations for all reactions.

13-38. How can each of the four hydrogen halides be prepared in moderately pure form in the laboratory? Write equations.

13-39. The German chemist Liebig is said to have prepared bromine several years before the discovery of this element, but to have failed to recognize it as a new element because of its close similarity in physical properties to ICl. How would you tell a sample of bromine from a sample of ICl?

13-40. It is stated in Section 13-9 that in hydrolysis of a binary compound the more electronegative element combines with hydrogen, and the less electronegative element combines with the OH group. Can you explain why this is to be expected? What would be the products of hydrolysis of ICl?