

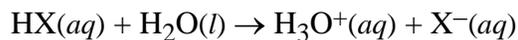
## Chapter 17

### THE GROUP 17 ELEMENTS: THE HALOGENS

#### Exercises

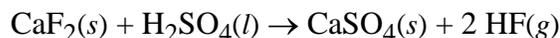
- 17.1 (a)  $\text{UO}_2(s) + 4 \text{HF}(g) \rightarrow \text{UF}_4(s) + 2 \text{H}_2\text{O}(l)$   
(b)  $\text{CaF}_2(s) + \text{H}_2\text{SO}_4(l) \rightarrow 2 \text{HF}(g) + \text{CaSO}_4(s)$   
(c)  $\text{SCl}_4(l) + 2 \text{H}_2\text{O}(l) \rightarrow \text{SO}_2(g) + 4 \text{HCl}(g)$   
(d)  $3 \text{Cl}_2(aq) + 6 \text{NaOH}(aq) \rightarrow \text{NaClO}_3(aq) + 5 \text{NaCl}(s) + 3 \text{H}_2\text{O}(l)$   
(e)  $\text{I}_2(s) + 5 \text{F}_2(g) \rightarrow 2 \text{IF}_5(s)$   
(f)  $\text{BrCl}_3(l) + 2 \text{H}_2\text{O}(l) \rightarrow 3 \text{HCl}(aq) + \text{HBrO}_2(aq)$
- 17.3 Fluorine has a very weak fluorine-fluorine bond; it is usually limited to one or two covalent bonds; its compounds with metals are often ionic when those of the comparable chlorides are covalent; it has an extremely high electronegativity and forms the strongest hydrogen bonds known; it tends to stabilize high oxidation states; the solubility of its metal compounds for a particular metal is often quite different than those of the other halides.
- 17.5 The reaction with nonmetals is strongly enthalpy-driven because weak fluorine-fluorine bonds are broken and strong bonds are formed between fluorine and other nonmetals.
- 17.7 The chemical equation is  
$$\text{I}_2(s) + 7 \text{F}_2(g) \rightarrow 2 \text{IF}_7(s)$$
Thus there is a decrease of seven moles of gas in this spontaneous reaction. Hence enthalpy decrease must be the driving force of the reaction.
- 17.9 The half-equation is:  
$$\frac{1}{2} \text{Cl}_2(aq) + e^- \rightarrow \text{Cl}^-(aq)$$
Because hydrogen ion does not appear in the half-equation, the reduction potential will not be pH sensitive.

17.11 In the ionization of a hydrohalic acid,



the H–X bond must be broken. The H–F bond is particularly strong, and as a result the equilibrium will tend to lie to the left and hydrofluoric acid will behave as a weak acid.

17.13 Chemical equation:



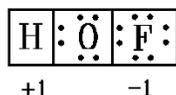
Mass of hydrogen fluoride =  $1.2 \times 10^{12}$  g

Moles of hydrogen fluoride =  $6.0 \times 10^{10}$  mol

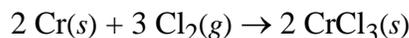
Moles of calcium sulfate =  $3.0 \times 10^{10}$  mol

Mass of calcium sulfate =  $4.1 \times 10^{12}$  g =  $4.1 \times 10^6$  tonne

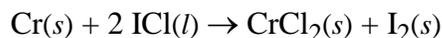
17.15 Oxygen has the unusual oxidation number of zero in this compound.



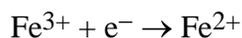
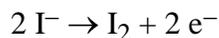
17.17 (a) To form the higher oxidation state of a metal, dichlorine should be used:



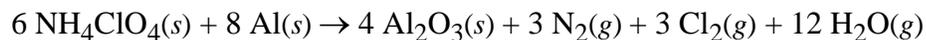
(b) To form the lower oxidation state of a metal, iodine monochloride should be used:



17.19 Iron(III) iodide will not be stable because iodide ion is a reducing agent, hence it will reduce iron(III) to iron(II):



17.21 The chemical equation is



Thus  $\Delta H = 12[\Delta H_f(\text{H}_2\text{O}(g))] + 4[\Delta H_f(\text{Al}_2\text{O}_3(s))] - 6[\Delta H_f(\text{NH}_4\text{ClO}_4(s))]$

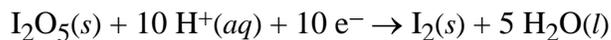
(because the other species are elements in their standard phases)

$$\Delta H = 12[-242 \text{ kJ}] + 4[-1676 \text{ kJ}] - 6[+295 \text{ kJ}]$$

$$= -7838 \text{ kJ}$$

It would also be a good propellant because it produces a large number of small gas molecules; thus it would have a high thrust per unit mass.

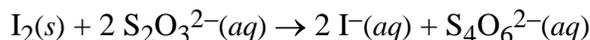
17.23 The half-equations for the first reaction,



give an overall equation of

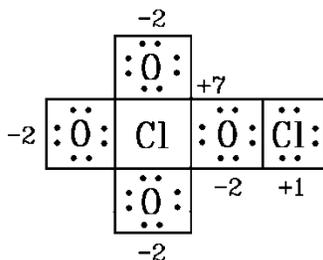


For the second reaction:

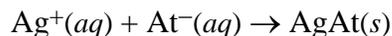


17.25 Three arguments can be used: first, that the sulfur atom is too small to accommodate six iodine atoms around it; second, that iodine is reducing, thus such a high oxidation state cannot be stabilized; and third, that the sulfur-iodine bond energy is not sufficient to provide an exothermic balance to the decrease in entropy that would result from consuming six moles of gas per mole of compound formed.

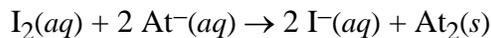
17.27 The central chlorine atom has a +7 oxidation number and the end chlorine has a +1 oxidation number. Both oxidation numbers are common for chlorine.



17.29 As iodine can almost be classed as a semimetal (for example, it is known in the +1 oxidation state), we would predict astatine to start to show some metallic properties; thus the diatomic element might be a significant electrical conductor. Like the other halogens, astatine should have a common oxidation state of  $-1$  and form an insoluble compound with silver ion:

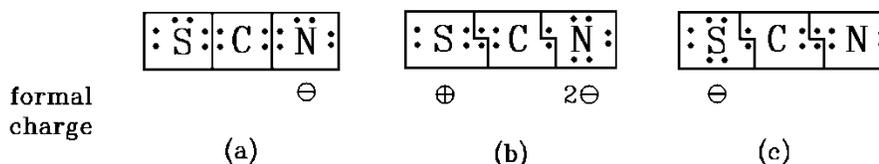


The compound should be insoluble in concentrated ammonia solution. All of the other halogens should displace its anion. For example, iodine should react as follows:

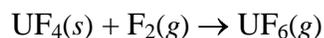
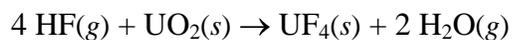
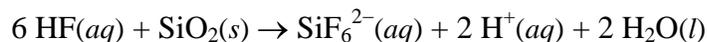
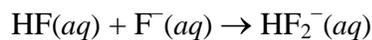
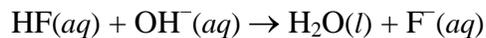
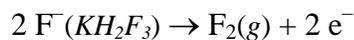
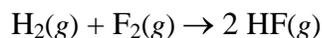
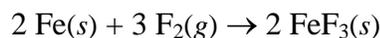
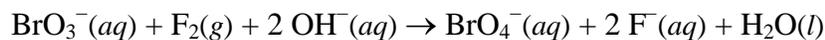
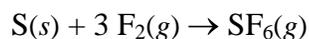
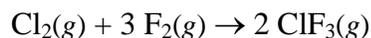


Astatine should form interhalogen compounds, such as AtF and AtI, in which astatine has a positive polarity. In fact, being so near the metal/nonmetal border, astatine will probably have a significant cation chemistry, forming, perhaps,  $\text{At}^+$  and  $\text{At}^{3+}$ .

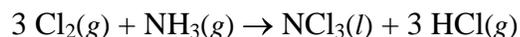
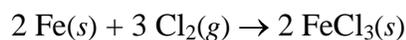
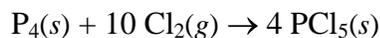
- 17.31 Structure (c), with the charge on the sulfur atom, must be the major contributor with, possibly, some small contribution from structure (a). In view of the high formal charge, contributions from structure (b) can be ignored.

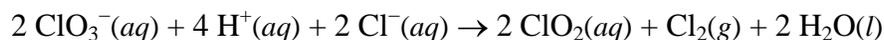
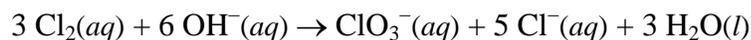
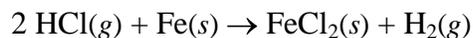
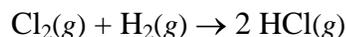
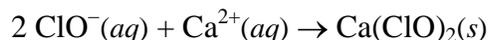
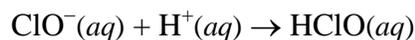


- 17.33 Fluorine:

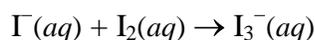
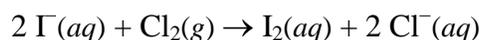
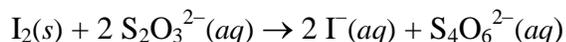
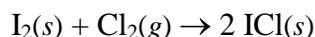


Chlorine:

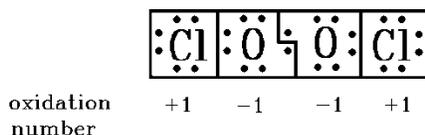




Iodine:



17.35 Chlorine oxidation state = +1, oxygen = -1.



17.37 The large low-charge iodide anion will stabilize the large low-charge cation.

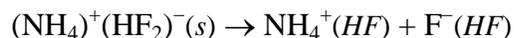
17.39 Bromine monofluoride, BrF, would be an analog of dichlorine, Cl<sub>2</sub>. Note that here we are using *combo* to indicate a combination of elements of the same group, but elements of period (*n*-1) and (*n*+1) as analogs of the element in period *n*.

17.41 (a) (CN)<sub>2</sub>; (b) AgCN, or Pb(CN)<sub>2</sub>, or Hg<sub>2</sub>(CN)<sub>2</sub>.

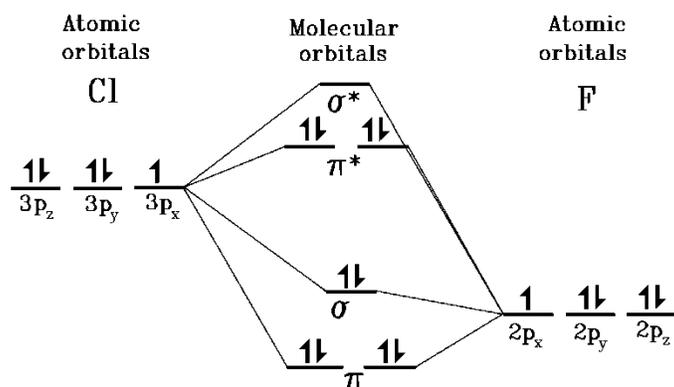
17.43 P(CN)<sub>3</sub>

## Beyond the Basics

17.45 The ammonium hydrogen fluoride may be decomposing and dissolving in the hydrogen fluoride produced.

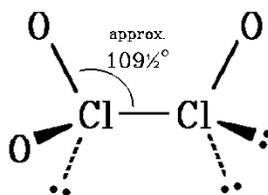
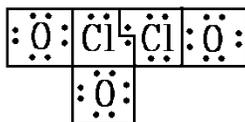


17.47 The bond order will be  $(3 - 2) = 1$ .



17.49 Dichlorine heptaoxide. It is the oxide in the higher oxidation state (with more oxygen atoms) that will be acidic.

17.51 Each chlorine atom will be approximately tetrahedrally coordinated, one chlorine with one lone pair and the other chlorine with two. Thus the bond angles will be approximately  $109\frac{1}{2}^\circ$ . Though the electron-dot structure depicts singly bonded oxygens, there is certainly multiple-bond character.

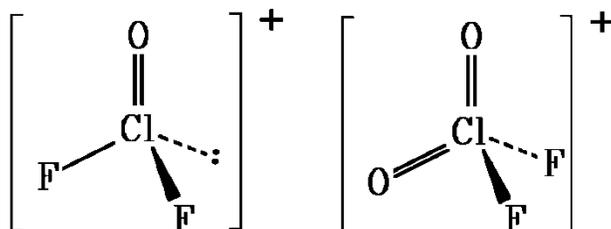
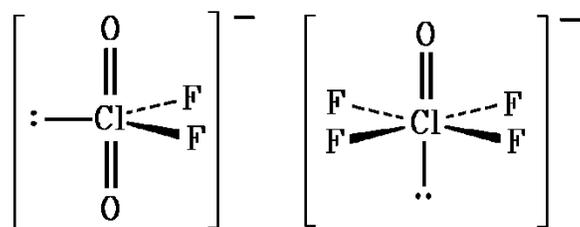


17.53 The perchlorate ion is a strong oxidizing agent, but it needs to be mixed with an oxidizable compound or element in order to have explosive properties. In ammonium perchlorate, the easily oxidizable ammonium ion is an integral part of the compound. Thus no additional component is required to cause a vigorous redox reaction.



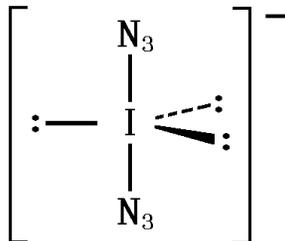
Nitrogen is oxidized from  $-3$  to  $0$ , chlorine is reduced from  $+7$  to  $0$ , and oxygen is oxidized from  $-2$  to  $0$ .

17.55 The structures follow. Single Cl–O bonds would be equally acceptable.



17.57  $\text{Tl}^+(\text{I}_3)^-$ . Iodide is a reducing agent and it would be expected to reduce thallium(III) to thallium(I).

- 17.59 (a) The azide ( $\text{N}_3^-$ ) ion, acts as a pseudohalide ion. Thus it can form a pseudo-interhalide ion by substituting for two of the iodine atoms in  $\text{I}_3^-$ , thus  $[\text{I}(\text{N}_3)_2]^-$ .



- (b) The azide must be of higher electronegativity than iodide because it is the less electronegative element that is the center of a cluster.
- (c) The iodide ion has seven electrons plus one from the negative charge. It will “share” one with each of the azide units, giving a total of ten electrons, or five electron pairs. Hence there will be a trigonal bipyramid electron-pair arrangement. Because the three lone pairs will occupy equatorial positions, the molecular shape will be linear.
- (d) The ion would be stabilized in the solid phase by a large cation such as rubidium or cesium.
- 17.61 (a)  $\text{ClF}_3(l) + \text{BF}_3(g) \rightarrow \text{ClF}_2^+(\text{ClF}_3) + \text{BF}_4^-(\text{ClF}_3)$
- (b)  $\text{ClF}_3(l) + \text{KF}(s) \rightarrow \text{K}^+(\text{ClF}_3) + \text{ClF}_4^-(\text{ClF}_3)$
- (c) In (a), the B–F bond is much stronger ( $613 \text{ kJ}\cdot\text{mol}^{-1}$ ) than the Cl–F bond ( $249 \text{ kJ}\cdot\text{mol}^{-1}$ ), so the boron can abstract a fluorine from the chlorine. In (b), the Cl–F bond strength must be greater than the energy needed to extract a fluoride ion from the potassium fluoride lattice.