

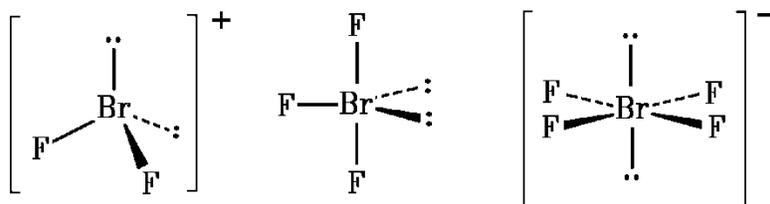
## Chapter 17

### THE GROUP 17 ELEMENTS: THE HALOGENS

#### Exercises

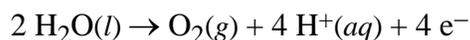
- 17.2 (a)  $\text{Pb}(s) + 2 \text{Cl}_2(g) \rightarrow \text{PbCl}_4(l)$   
(b)  $\text{Mg}(s) + 2 \text{HCl}(aq) \rightarrow \text{MgCl}_2(aq) + \text{H}_2(g)$   
(c)  $\text{ClO}^-(aq) + \text{SO}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{SO}_4^{2-}(aq) + \text{Cl}^-(aq) + 2 \text{H}^+(aq)$   
(d)  $4 \text{KClO}_3(l) \rightarrow \text{KCl}(s) + 3 \text{KClO}_4(s)$   
(e)  $\text{IBr}(s) + \text{H}_2\text{O}(l) \rightarrow \text{HBr}(aq) + \text{HIO}(aq)$   
(f)  $\text{P}(s) + 3 \text{ICl}(l) \rightarrow \text{PCl}_3(l) + \frac{3}{2} \text{I}_2(s)$

- 17.4 (a) V-shaped; (b) T-shaped; (c) square planar.

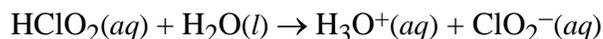


- 17.6 These would both be odd-proton odd-neutron nuclei. There are only four stable examples of these isotopes in the whole periodic table.

- 17.8 Difluorine cannot be produced electrolytically from aqueous solution because the potential needed for the oxidation of water is less than that needed for the oxidation of the fluoride ion. Thus dioxygen would be produced instead:

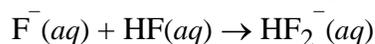


- 17.10 Chlorous acid is a weak acid; hence in acidic solution, the equilibrium lies to the left:



As a result,  $\text{HClO}_2$  is the predominant acid species.

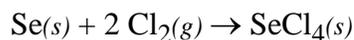
17.12 In concentrated hydrofluoric acid, fluoride ion reacts with un-ionized hydrofluoric acid to give the  $\text{HF}_2^-$  ion, resulting in greater ionization:



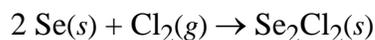
17.14 As low-charge-density cations stabilize low-charge anions, large, low-charge-density potassium ion is likely to form a stable solid compound with the hydrogen difluoride ion.

17.16 Unlike nitric acid, hydrochloric acid is not oxidizing.

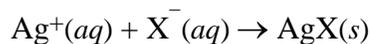
17.18 (a) To form the higher oxidation state compound of a nonmetal, excess dichlorine should be used:



(b) To form the lower oxidation state of a nonmetal, an excess of that element should be used:



17.20 The common test for distinguishing chloride, bromide, and iodide ions involves addition of silver ion to give precipitates:



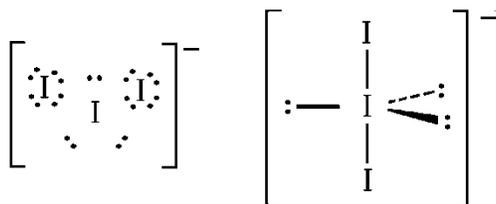
Silver chloride is white and reacts with dilute ammonia solution:



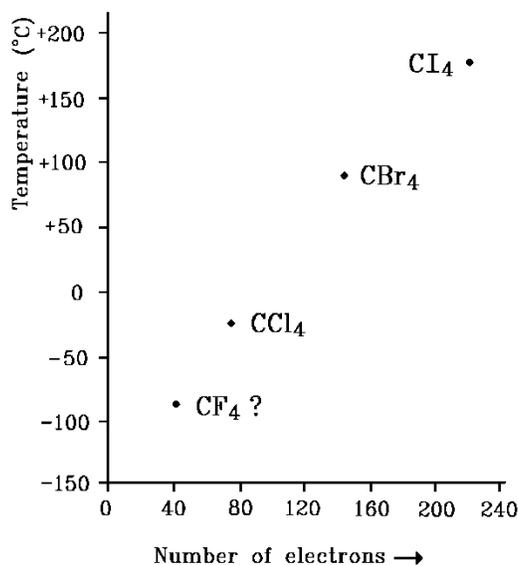
Silver bromide reacts with concentrated ammonia in a similar manner; while silver iodide does not react even with concentrated ammonia.

(Descriptions of the halogen displacement tests would also be acceptable).

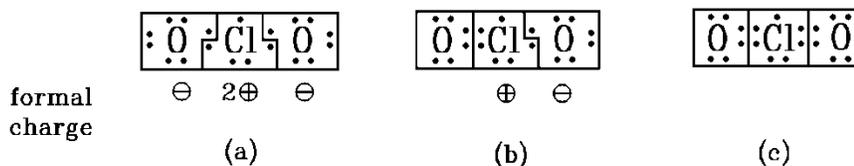
17.22 The  $\text{I}_3^-$  ion will be linear as a result of the three equatorial lone pairs.



- 17.24 The only intermolecular forces for these nonpolar molecules are dispersion forces. These depend upon the number of electrons in a molecule. On that basis, by graph or calculation, the melting point of carbon tetrafluoride should be about  $-90^{\circ}\text{C}$ —in fact, it is much lower, at  $-187^{\circ}\text{C}$ .



- 17.26 The two double-bond structures would be preferred according to formal charge considerations.

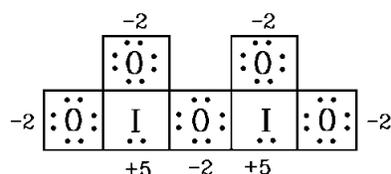


- 17.28 (a) Sodium hypochlorite is used for bleaching wood pulp and textiles and as a household bleach and disinfectant.  
 (b) Chlorine dioxide is used to bleach flour and wood pulp.  
 (c) Ammonium perchlorate is used as the oxidizer in solid-fuel rockets.  
 (d) Iodine monochloride is used as a reagent to test for degree of unsaturation in oils and fats.

17.30 Cyanide ion is considered a pseudohalogen for the following reasons: cyanide ion is the conjugate base of a weak acid, hydrocyanic acid, which is analogous to the fluoride ion forming hydrofluoric acid; it can be oxidized to  $(\text{CN})_2$ , which is analogous to an elemental halogen; the anion forms white precipitates with silver ion, lead(II) ion, and mercury(I) ion, like chloride ion; the silver thiocyanate reacts with dilute ammonia solution, like silver chloride; it forms pseudointerhalogen compounds, such as  $\text{BrCN}$ ; and it forms complexes with metal ions that have formulas analogous to those of the chloride complexes.

17.32 The fluoride ion replaces the hydroxide ion in the hydroxyapatite structure to give the tougher compound,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ .

17.34 The bonding is different because iodine has two more valence electrons. Thus there is a lone pair on each iodine atom. As a result, each iodine has a tetrahedral environment. The terminal iodine-oxygen bonds are shown as single bonds, though they probably have multiple bond character.



Oxidation states: iodine = +5; oxygen (bridging and terminal) = -2.

17.36 Because the fluoride ion is quite small, only four fluoride ions can pack around an ammonium ion. Six ammonium ions can pack around the larger chloride ion.



17.40 (a) Hydrocyanic acid is a weak acid like hydrofluoric acid.  
 (b) Silver cyanide reacts with ammonia to give the soluble diamminesilver ion, as does the silver chloride; or, cyanogen reacts with water to give the cyanide and cyanate ions in a parallel reaction to that of chlorine; or, cyanide forms complexes such as  $[\text{Cu}(\text{CN})_4]^{2-}$  which parallel their chloride counterparts.

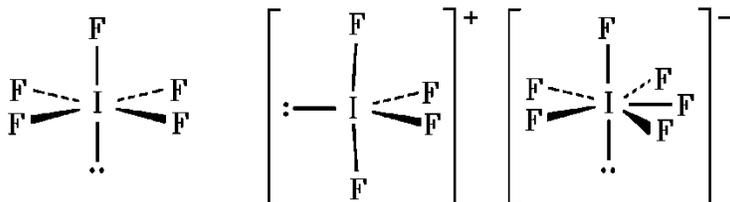
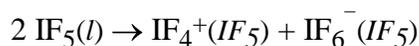
(c) Cyanide ion is oxidized by copper(II) ion to give cyanogen, just as iodide ion is oxidized to iodine.

17.42 This would have the linear structure  $\text{N}\equiv\text{C}-\text{C}\equiv\text{N}$ . It is probable that the  $\pi$ -bond system extends across the whole molecule, increasing the bond order across the C–C link while slightly weakening the  $\text{C}\equiv\text{N}$  bond.



### Beyond the Basics

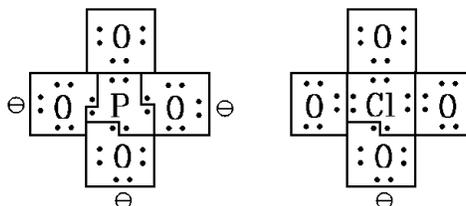
17.44 The self-ionization reaction would be:



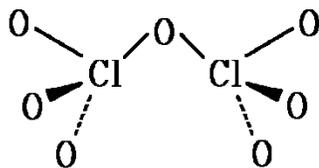
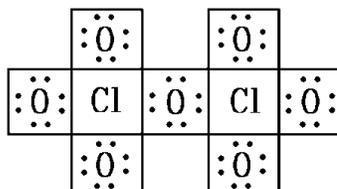
The  $\text{IF}_5$  molecule is square-based pyramidal, the  $\text{IF}_4^+$  ion is seesaw shaped, and the  $\text{IF}_6^-$  ion is octahedral. The  $\text{IF}_4^+$  will be a Lewis acid and  $\text{IF}_6^-$  will be the Lewis base. Looking at the reverse reaction,  $\text{IF}_4^+$  accepts a fluoride ion, and thus it accepts an electron pair; while  $\text{IF}_6^-$  donates a fluoride ion, and thus it donates an electron pair.

17.46 To solve this, we can use an energy cycle that shows that the bond energy of the dichlorine ion is 405 kJ, compared to 240 kJ for the molecule. This indicates, as would be expected from comparison with the fluorine molecular orbital diagram, that the ionized electron is lost from an antibonding orbital, resulting in an increased bond order of  $1\frac{1}{2}$ .

- 17.48 As the preferred formal charge structure for the phosphate ion contains one double bond and that of perchlorate contains three, then sulfate should contain two. This would give an average S–O bond order of  $1\frac{1}{2}$ .



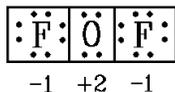
- 17.50 (a) Using the calculation method  $2[\text{Cl}] + 7[\text{O}] = 0$ ,  $[\text{Cl}] = +7$ .  
 (b) The bond angle about the oxygen will be about  $109\frac{1}{2}^\circ$ . Each chlorine-oxygen bond is shown as a single bond, but there will certainly be some double bond character.



- (c)  $\text{Cl}_2\text{O}_7(l) + \text{H}_2\text{O}(l) \rightarrow 2 \text{HClO}_4(l)$  (or  $(aq)$ )  
 (d)  $\text{Mn}_2\text{O}_7$  (using the  $(n)$  and  $(n+10)$  group similarity)
- 17.52 (a)  $(\text{CN})_2(aq) + 2 \text{OH}^-(aq) \rightarrow \text{HCN}(aq) + \text{HCNO}(aq)$   
 (b)  $\text{NCS}^-(aq) \rightarrow (\text{NCS})_2(aq) + 2 \text{e}^-$   
 $\text{MnO}_4^-(aq) + 8 \text{H}^+(aq) + 5 \text{e}^- \rightarrow \text{Mn}^{2+}(aq) + 4 \text{H}_2\text{O}(l)$
- 17.54  $\text{I}^{x+} + 3 \text{I}^- + 3 \text{e}^- \rightarrow 2 \text{I}_2(g)$

Thus  $x$  must be 3, and the formula must be  $\text{ICl}_3$ .

- 17.56 Oxygen, being the second most electronegative element, usually has a negative oxidation state. It is only with fluorine that oxygen has a positive oxidation state. Fluorine would not form other oxides such as one analogous to  $\text{Cl}_2\text{O}_7$ . In  $\text{Cl}_2\text{O}_7$ , chlorine has an oxidation state of +7. Fluorine cannot form compounds in which it has positive oxidation states.



- 17.58  $2 \text{Cl} + 2 \text{O}_3 \rightarrow 2 \text{ClO} + 2 \text{O}_2$   
 $\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M}^*$   
 $\text{Cl}_2\text{O}_2 + h\nu \rightarrow \text{ClOO} + \text{Cl}$   
 $\text{ClOO} \rightarrow \text{Cl} + \text{O}_2$   
 $2 \text{O}_3 + h\nu \rightarrow 3 \text{O}_2$

Cl is the catalyst; ClO,  $\text{Cl}_2\text{O}_2$ , and ClOO are intermediates.

- 17.60 (a)  $\text{I}_2(s) + \text{Cl}_2(g) \rightarrow 2 \text{ICl}(g)$

- (b) Energy input:

$$\Delta H_{\text{sublimation}}(\text{I}_2) + \text{B.E.}(\text{I-I}) + \text{B.E.}(\text{Cl-Cl}) \\ = [62 + 149 + 240] \text{ kJ}\cdot\text{mol}^{-1} = 451 \text{ kJ}\cdot\text{mol}^{-1}$$

Energy released:

$$2 \times \text{B.E.}(\text{I-Cl}) = 2x$$

$$\Delta H_{\text{f}}^{\circ}(\text{ICl})^* = +18 \text{ kJ}\cdot\text{mol}^{-1} = (+451 \text{ kJ}\cdot\text{mol}^{-1}) - 2x$$

\*(from Appendix table)

$$2x = 433 \text{ kJ}\cdot\text{mol}^{-1}$$

$$x = 216 \text{ kJ}\cdot\text{mol}^{-1}$$

- (c)  $\Delta G = \Delta H - T\Delta S$

$$T\Delta S = \Delta H - \Delta G = (+18) - (-5) \text{ kJ}\cdot\text{mol}^{-1} = +23 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta S \text{ (at 298 K)} = +77 \text{ kJ}\cdot\text{mol}^{-1}$$

One would expect a positive value of entropy change as there are two moles of gas in the product and only one in the reactant. The entropy has to be positive for this reaction to occur spontaneously because the enthalpy term is positive. Thus entropy has to be the driving force.

