

# Group 16—The Oxygen Family

- The first two members of Group 16, oxygen and sulfur, are essential for life.
- The heavier members of the group, tellurium and polonium, are both metalloids.

Group 16  
The Oxygen  
Family

Oxygen	8	O
Sulfur	16	S
Selenium	34	Se
Tellurium	52	Te
Polonium	84	Po

Except for oxygen, there are patterns in the oxidation states of the Group 16 elements. We find all of the even-numbered oxidation states from +6, through +4 and +2, to -2. The stability of the -2 and +6 oxidation states decreases down the group, whereas that of the +4 state increases. As happens in many



## Representative Elements

### Dioxygen

Dioxygen is a colorless, odorless gas that condenses to a pale blue liquid.

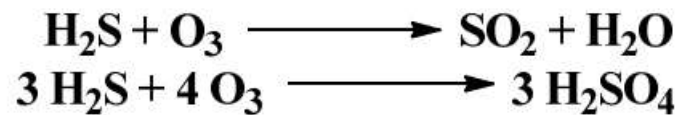
- Ozone, a less common form of oxygen, is formed in the upper atmosphere through the action of electricity during thunderstorms.
- The presence of ozone is important because it shields living organisms from some harmful radiation from the Sun.

A convenient way to generate trioxxygen is to pass a stream of dioxygen through a 10- to 20-kV electric field. This field provides the energy necessary for the reaction

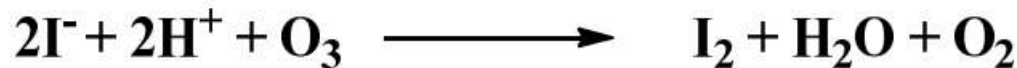


## الاستدلال على قوة الاكسدة للاوزون

يؤكسد الكبريت الى الكبريتات



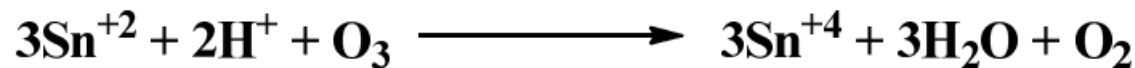
يؤكسد آيون اليوديد في الوسط الحامضي الى اليود



يؤكسد الحديدوز في الوسط الحامضي الى الحديديك

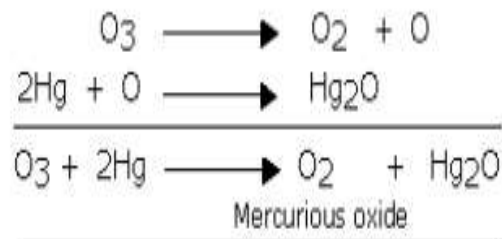


والقصديروز الى قصديريك



## REACTION WITH WITH MERCURY

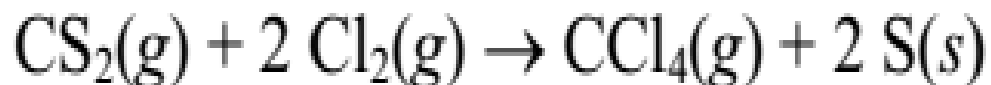
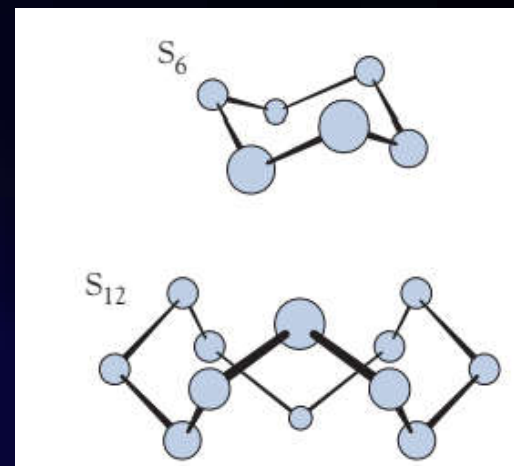
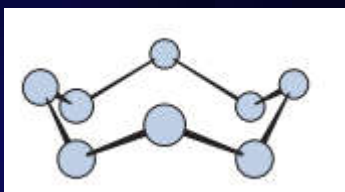
When ozone is passed through mercury, it loses its meniscus and sticks to the glass due to the formation of mercurous oxide. This is called tailing of mercury. The meniscus can be restored by shaking it with water.



## Representative Elements




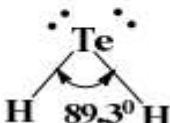
Sulfur is a solid, yellow nonmetal.

- Large amounts of sulfur are used to manufacture sulfuric acid, one of the most commonly used chemicals in the world.
- Sulfuric acid is a combination of sulfur, hydrogen, and oxygen.
- It is used in the manufacture of paints, fertilizers, detergents, synthetic fibers, and rubber.



## Representative Elements

الهيدريدات:

			
m.p.°C    0.0	-85.5	-66.0	-51.2
b.p.°C    100.0	-60.5	-41.0	-20.0

59

The hydrogen sulfide molecule has a V-shaped structure, as would be expected for an analog of the water molecule. However, as we descend the group, the bond angles in their hydrides decrease (Table 16.9). The variation of bond angle can be explained in terms of a decreasing use of hybrid orbitals by elements beyond Period 2. Hence, it can be argued that the bonding in hydrogen selenide involves *p* orbitals only. This reasoning is the most commonly accepted explanation, because it is consistent with observed bond angles in other sets of compounds.

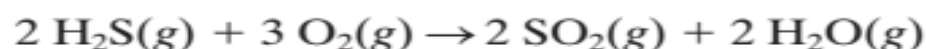
**TABLE 16.9** Bond angles of three Group 16 hydrides

Hydride	Bond angle
H <sub>2</sub> O	104 $\frac{1}{2}$ °
H <sub>2</sub> S	92 $\frac{1}{2}$ °
H <sub>2</sub> Se	90°

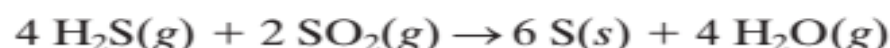
prepared in the laboratory by reacting a metal sulfide with a dilute acid, such as iron(II) sulfide with dilute hydrochloric acid:



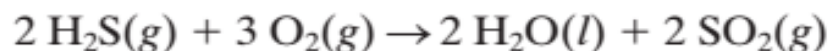
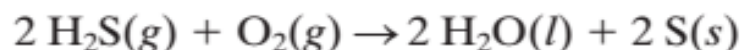
lead(II) acetate is converted to black lead(II) sulfide:



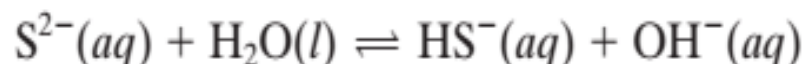
The sulfur dioxide produced then reacts with the remaining two-thirds of the hydrogen sulfide to give elemental sulfur:



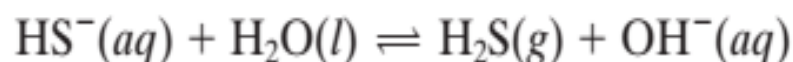
Hydrogen sulfide burns in air to give sulfur or sulfur dioxide, depending on the gas-to-air ratio:



## Sulfides



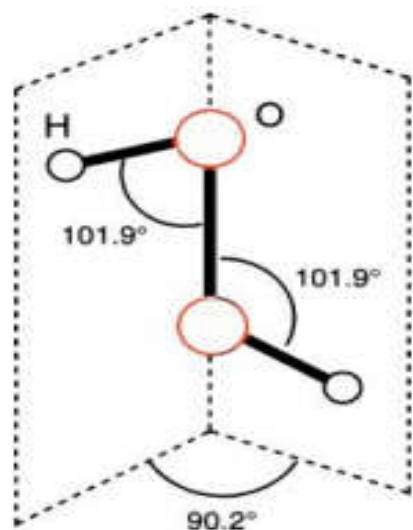
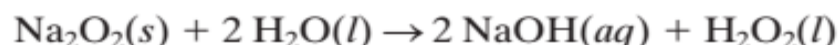
There is enough hydrolysis of the hydrogen sulfide ion, in turn, to give the solution a strong odor of hydrogen sulfide:



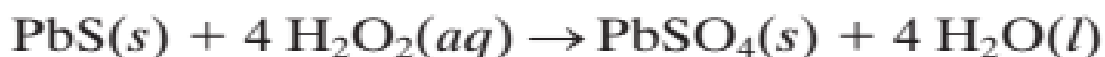


## Hydrogen Peroxide

A solution of hydrogen peroxide can be prepared in the laboratory by the reaction of sodium peroxide with water:



Hydrogen peroxide will oxidize iodide ion to iodine and reduce permanganate ion in acid solution to manganese(II) ion. Hydrogen peroxide has an important application to the restoration of antique paintings. One of the favored white pigments was white lead, a mixed carbonate-hydroxide,  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ . Traces of hydrogen sulfide cause the conversion of this white compound to black lead(II) sulfide, which discolors the painting. Application of hydrogen peroxide oxidizes the lead(II) sulfide to white lead(II) sulfate, thereby restoring the correct color of the painting:



## Halides

### Oxygen Halides

The six known oxygen fluorides:

OF<sub>2</sub>  
O<sub>2</sub>F<sub>2</sub>  
O<sub>3</sub>F<sub>2</sub>  
O<sub>4</sub>F<sub>2</sub>  
O<sub>5</sub>F<sub>2</sub>  
O<sub>6</sub>F<sub>2</sub>

<+1

S<sub>n</sub>Cl<sub>2</sub> (n = 3-8), S<sub>n</sub>Br<sub>2</sub>  
(n = 3-8)

+1

S<sub>2</sub>F<sub>2</sub>, S<sub>2</sub>Cl<sub>2</sub>, S<sub>2</sub>Br<sub>2</sub>, S<sub>2</sub>I<sub>2</sub>

+2

SF<sub>2</sub>, SCl<sub>2</sub>

+4

SF<sub>4</sub>, SCl<sub>4</sub>

+5

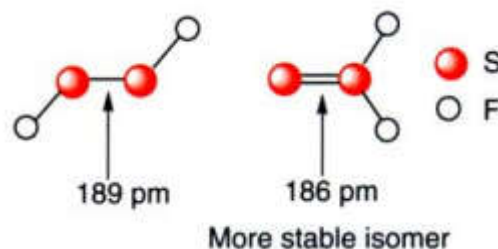
S<sub>2</sub>F<sub>10</sub>

+6

SF<sub>6</sub>

Oxygen forms six fluorides, which have chains of from one to six oxygen atoms, terminated by fluorines. Since fluorine always has a negative oxidation state (being the most electronegative element), these oxygen fluorides are rare examples of compounds with oxygen in positive oxidation states.

### Sulfur Halides



species. S<sub>2</sub>Cl<sub>2</sub> and S<sub>2</sub>Br<sub>2</sub> are formed by direct combination of the elements (equation 8.20).



The only stable sulfur dihalide is the bent SCl<sub>2</sub>, which disproportionates to give S<sub>2</sub>Cl<sub>2</sub> and Cl<sub>2</sub> (equation 8.21). SF<sub>2</sub> is even less stable.

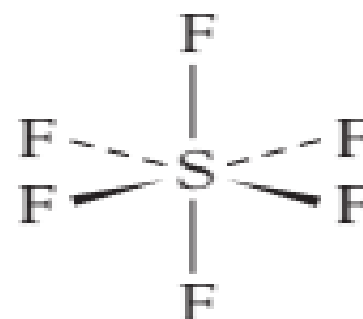
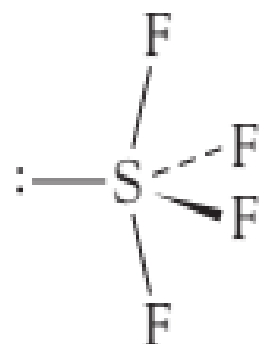




Sulfur(IV) halides are restricted to  $\text{SF}_4$  and  $\text{SCl}_4$  (the latter being the less stable, and only occurring in the solid state where it is thought to exist in an ionic form as  $\text{SCl}_3^+\text{Cl}^-$ ).  $\text{SF}_4$  has a structure derived from a trigonal bipyramid; see Worked Problem 1.6. Although highly moisture-sensitive (equation 8.22), it is finding use as a fluorinating agent in organic chemistry.



In contrast to the high reactivity of  $\text{SF}_2$  and  $\text{SF}_4$ , **sulfur hexafluoride** ( $\text{SF}_6$ ) is unreactive. The hydrolysis of  $\text{SF}_6$  is *thermodynamically* very favourable, indicated by the large, negative  $\Delta G^\circ$  value ( $-301 \text{ kJ mol}^{-1}$ ) calculated for the hydrolysis reaction in equation 8.23.

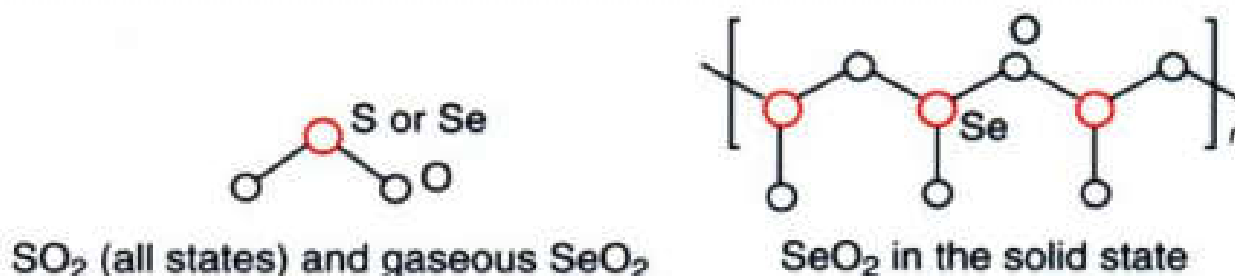


## Dioxides, EO<sub>2</sub>

The dioxides EO<sub>2</sub> are known for S, Se, Te and Po, and are formed by heating the elements in air, for example sulfur (equation 8.24).



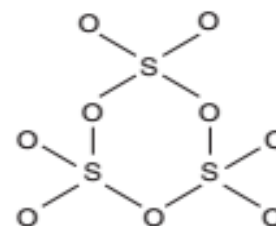
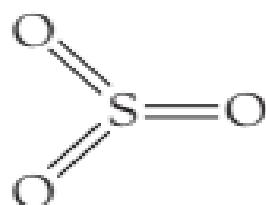
The dioxides have very different structures. SO<sub>2</sub> is a covalent molecular substance, SeO<sub>2</sub> has an infinite covalent chain structure in the solid state (and a molecular SO<sub>2</sub>-type structure in the gas phase) (Figure 8.6), while TeO<sub>2</sub> and PoO<sub>2</sub> have ionic structures. The different structures reflect the increasing metallic character of the elements going down the group, and the tendency for only the light elements (Se and particularly S) to engage in E=O  $\pi$ -bonding. For SeO<sub>2</sub>, some  $\pi$ -bonding is sacrificed to provide extra  $\sigma$ -bonding; the same reasons account for the different structures



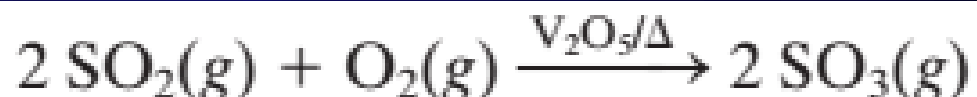
يحضر SO<sub>2</sub> من تسخين مزيج حامض الكبريتيك المركز مع خراطة النحاس وهو مادة مهمة صناعياً



## Trioxides, $\text{EO}_3$



important oxide, sulfur trioxide, a colorless liquid at room temperature. The liquid and gas phases contain a mixture of sulfur trioxide,  $\text{SO}_3$ , and trisulfur nonaoxide,  $\text{S}_3\text{O}_9$  (Figure 16.16). The liquid freezes at  $16^\circ\text{C}$  to give crystals of the trimer trisulfur nonaoxide. The trimer is isoelectronic and isostructural with the polyphosphate ion,  $(\text{P}_3\text{O}_9)^{3-}$ , and the polysilicate ion,  $(\text{Si}_3\text{O}_9)^{6-}$ .

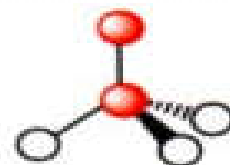


### Sulfurous, Selenous and Tellurous acids, $\text{H}_2\text{EO}_3$

Sulfur dioxide is very soluble in water and dissolves largely without reaction, forming an acidic solution commonly referred to as 'sulfurous acid' ( $\text{H}_2\text{SO}_3$ ). The free acid has never been isolated, and is either absent or present in only trace amounts in aqueous  $\text{SO}_2$  solutions.<sup>2</sup>

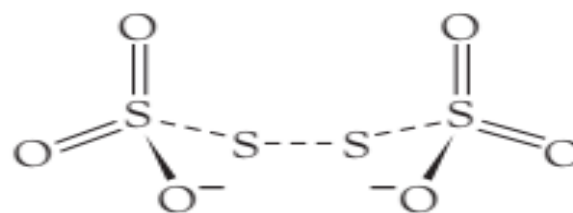


sulfite  $\text{SO}_3^{2-}$



thiosulfate  $\text{S}_2\text{O}_3^{2-}$

Selenium dioxide and tellurium dioxide behave similarly, although the solutions are less acidic than  $\text{H}_2\text{SO}_3$ . A solution of  $\text{SO}_2$ ,  $\text{SeO}_2$  or  $\text{TeO}_2$  in aqueous hydroxide solutions gives  $\text{EO}_3^{2-}$  or  $\text{HEO}_3^-$  anions. Sulfite reacts with sulfur on heating to give the well-known **thiosulfate** anion (equation 8.27).



Mixing cold solutions of thiosulfate ion and iron(III) ion gives a characteristic deep purple complex ion:

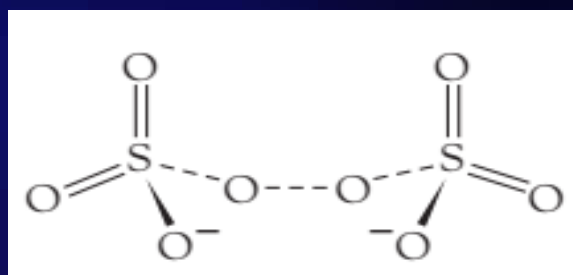
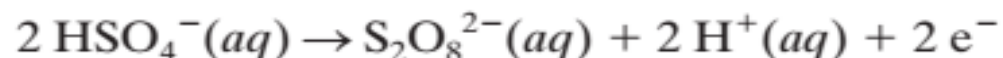


When warmed, this bis(thiosulfato)ferrate(III) ion,  $[\text{Fe}(\text{S}_2\text{O}_3)_2]^-$ , undergoes a redox reaction to give the iron(II) ion and the tetrathionate ion:



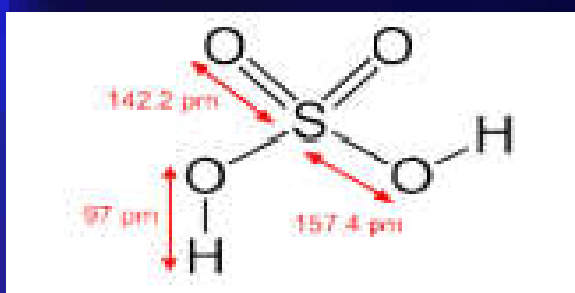
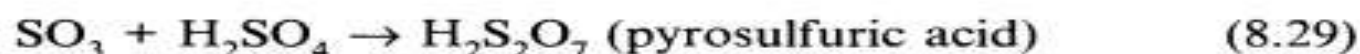
### Peroxodisulfates

Although the sulfate ion contains sulfur in its highest possible oxidation state of +6, it can be oxidized electrolytically to the peroxodisulfate ion by using smooth platinum electrodes, acidic solution, and high current densities. These conditions favor oxidations that do not produce gases such as the competing oxidation of water to dioxygen:



# Sulfuric, Selenic and Telluric Acids

**Sulfuric acid** is well known and is prepared by the oxidation of sulfur dioxide to sulfur trioxide (Section 8.5.2), followed by hydrolysis of the  $\text{SO}_3$  in sulfuric acid to give pyrosulfuric acid (often called **oleum**), which is then hydrolysed (equations 8.28–8.30).



The purpose of dissolving the  $\text{SO}_3$  in  $\text{H}_2\text{SO}_4$  is to moderate the violent reaction which would occur between  $\text{SO}_3$  and water.



Sulfuric acid and the sulfate anion ( $\text{SO}_4^{2-}$ ) are difficult to reduce, and sulfuric acid is a very strong acid ( $\text{p}K_a < 0$ ).

**Selenic acid**,  $\text{H}_2\text{SeO}_4$ , is similar to sulfuric acid; however, the corresponding acid containing tellurium(VI) is the diprotic hexahydroxy acid,  $\text{Te}(\text{OH})_6$ . This occurs formally by addition of water to  $\text{Te}=\text{O}$  groups, and thus tellurium is showing the characteristic increase in its coordination number observed for other heavy p-block elements, such as iodine