Chapter 19

THE GROUP VIB(16) ELEMENTS: SULFUR, SELENIUM, TELLURIUM, AND POLONIUM

19-1 Introduction

The position of these elements in the periodic table has been discussed in Chapter 8, and some properties are listed in Table 8-6. The elements of Group VIB(16) bear little resemblance to oxygen for the following reasons:

1. Sulfur, selenium, tellurium, and polonium have lower electronegativities than oxygen; consequently, their compounds have less ionic character. The relative stabilities of their bonds to other elements are also different. In particular, the importance of hydrogen bonding is drastically lowered. Only very weak S- - -H—S bonds exist, and H_2S is totally different from H_2O (Chapter 7).

2. For sulfur particularly, as in other third-row elements, there is multiple $d\pi$–$p\pi$ bonding, but little if any $p\pi$–$p\pi$ bonding. The short S—O distances in SO_4^{2-} (where *s* and *p* orbitals are used in σ bonding) is a result of multiple $d\pi$–$p\pi$ bond character. The latter arises from the flow of electrons from filled $p\pi$ orbitals on O atoms to empty $d\pi$ orbitals on S atoms.

3. The valence for S, Se, Te, and Po atoms is not confined to 2, and *d* orbitals can be utilized to form more than four bonds to other elements. Examples are SF_6 and $Te(OH)_6$.

4. Sulfur has a strong tendency to catenation, equaled or exceeded only by carbon. Sulfur forms compounds for which there are no known O, Se, or Te analogs. Examples are polysulfide ions, S_n^{2-}, polythionate ions, $[O_3S—S_n—SO_3]^{2-}$, and compounds of the type XS_nX, where X = H, Cl, CN, or NR_2.

The changes in the properties of compounds on going from S to Po can be associated with the increasing size of the atoms and with the decreasing electronegativity, from top to bottom in the group. Some examples of trends in properties of compounds that arise for these reasons are

1. The decreasing stability of the hydrides H_2E.
2. The increasing tendency to form complex ions such as $SeBr_6^{2-}$.
3. The appearance of metallic properties for Te and Po atoms. Thus the oxides MO_2 are ionic and basic, reacting with HCl to give the chlorides.

19-2 Occurrence and Reactions of the Elements

Sulfur occurs widely in nature as the element, as H_2S and SO_2, in metal sulfide ores, and as sulfates [e.g., gypsum and anhydrite ($CaSO_4$), magnesium sulfate, and so on]. Sulfur is obtained on a vast scale from natural hydrocarbon gases such as those in Alberta, Canada, which contain up to 30% H_2S; this is removed by interaction with SO_2, which is obtained from burning sulfur in air.

$$S + O_2 = SO_2 \tag{19-2.1}$$

$$2\ H_2S + SO_2 = 3\ S + 2\ H_2O \tag{19-2.2}$$

Selenium and tellurium are less abundant but frequently occur as selenide and telluride minerals in sulfide ores, particularly those of Ag and Au. They are recovered from flue dusts from combustion chambers for sulfide ores.

Polonium occurs in U and Th minerals as a product of radioactive decay series. The most accessible isotope, ^{210}Po (α, 138.4 days), can be made in gram quantities by irradiation of Bi in nuclear reactors.

$$^{209}Bi(n,\ \gamma)^{210}Bi \xrightarrow{\beta^-} {}^{210}Po \tag{19-2.3}$$

The Po can be separated by sublimation on heating. It is intensely radioactive and special handling techniques are required. The chemistry resembles that of Te but is somewhat more "metallic."

The physical properties and structures of the elements have been described (Chapter 8). On melting, S_8 first gives a yellow, transparent, mobile liquid that becomes dark and increasingly viscous above about 160 °C. The maximum viscosity occurs about 200 °C, but on further heating the mobility increases until the boiling point (444.6 °C), where the liquid is dark red. The "melting point" of S_8 is actually a decomposition point. Just after melting, rings with an average of 13.8 sulfur atoms are formed and at higher temperature, still larger rings form. Then in the high viscosity region there are giant macromolecules that are probably chains with radical ends. At higher temperatures, highly colored S_3 and S_4 molecules are present to the extent of 1–3% at the boiling point. The nature of the physical changes and of the species involved are by no means fully understood.

Sulfur vapor contains S_8 and at higher temperatures S_2 molecules. The latter, like O_2, are paramagnetic with two unpaired electrons, and account for the blue color of the hot vapor.

Cyclosulfurs other than S_8, with ring sizes from S_6 to S_{20}, can be prepared by specific synthetic routes. These compounds are all unstable in solution relative to S_8, but solutions of S_8 do contain, at equilibrium, about 0.3% S_6 and 0.8% S_7, both of which are much more reactive than S_8.

The elements S, Se, and Te burn in air on heating to form the dioxides; they also react on heating with halogens, most metals, and nonmetals. They are attacked by hot oxidizing acids like H_2SO_4 or HNO_3.

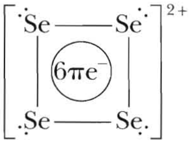
In oleums (Section 7-11), S, Se, and Te dissolve to give highly colored solutions that contain cations in which the element is in a fractional oxidation state. Salts of the cations M_4^{2+}, M_8^{2+}, and M_{16}^{2+} have been obtained by selective oxidation of the elements with SbF_5 or AsF_5 in liquid HF. For example,

$$S_8 + 3\ SbF_5 = S_8^{2+} + 2\ SbF_6^- + SbF_3 \tag{19-2.4}$$

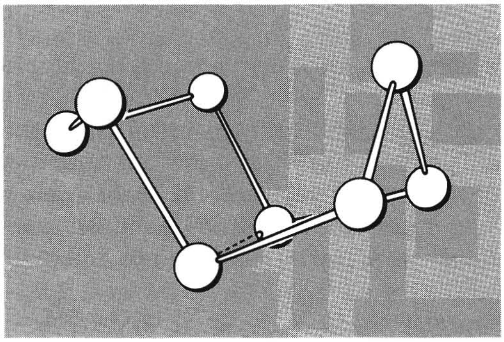
or by reactions in molten $AlCl_3$, for example,

$$7\ Te + TeCl_4 + 4\ AlCl_3 = 2\ Te_4^{2+} + 4\ AlCl_4^- \tag{19-2.5}$$

The S_4^{2+}, Se_4^{2+}, and Te_4^{2+} ions are square (Structure 19-I) and there is probably a six π-electron quasiaromatic system. The green Se_8^{2+} ion has a ring structure (Structure 19-II). The S_{16}^{2+} and Se_{16}^{2+} ions have two M_8 rings joined together.



19-I



19-II

The reaction of sulfur with the double bonds of natural and synthetic rubbers (a process called vulcanization) is of great technical importance. It leads to formation of S bridges between carbon chains and, hence, to strengthening of rubber.

All reactions of S_8 must involve initial ring opening to give sulfur chains or chain compounds. Many involve nucleophilic reactants, for example,

$$S_8 + 8\ CN^- \longrightarrow 8\ SCN^- \tag{19-2.6}$$

$$S_8 + 8\ Na_2SO_3 \longrightarrow 8\ Na_2S_2O_3 \tag{19-2.7}$$

$$S_8 + 8(C_6H_5)_3P \longrightarrow 8(C_6H_5)_3PS \tag{19-2.8}$$

Such reactions proceed by a series of steps such as

$$S_8 + CN^- \longrightarrow SSSSSSSSCN^- \tag{19-2.9}$$

$$S_6{-}S{-}SCN^- + CN^- \longrightarrow S_6SCN^- + SCN^- \quad \text{and so on} \tag{19-2.10}$$

Sulfur–sulfur bonds occur in a variety of compounds, and —S—S— bridges are especially important in certain enzymes and other proteins.

19-3 Hydrides: EH_2

These compounds are obtained by the action of acids on metal sulfides, selenides, or tellurides. The hydrides are extremely poisonous gases with revolting odors. The toxicity of H_2S far exceeds that of HCN. The thermal stability and bond strengths decrease down the series, whereas the acidity in water increases.

Hydrogen sulfide dissolves in water to give a solution about 0.1 *M* at 1 atm. Its dissociation constants are

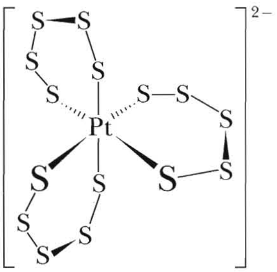


Figure 19-1 A complex ion of Pt^{IV} in which the three S_5^{2-} ligands are each bidentate.

$$H_2S + H_2O = H_3O^+ + SH^- \qquad K = 1 \times 10^{-7} \qquad (19\text{-}3.1)$$

$$SH^- + H_2O = H_3O^+ + S^{2-} \qquad K = \sim 10^{-14} \qquad (19\text{-}3.2)$$

Owing to this small second dissociation constant, essentially only SH^- ions are present in solutions of ionic sulfides, and S^{2-} occurs only in very alkaline solutions (>8 *M* NaOH) as shown in Equation 19-3.3.

$$S^{2-} + H_2O = SH^- + OH^- \qquad K = \sim 1 \qquad (19\text{-}3.3)$$

The compounds H_2S_2 to H_2S_6 are generally known as sulfanes; they contain —SS— to —SSSSSS— chains. These compounds can be obtained by reactions such as

$$2\ H_2S(\ell) + S_nCl_2 = 2\ HCl(g) + H_2S_{n+2}(\ell) \qquad (19\text{-}3.4)$$

The anions of the sulfanes (polysulfides, S_n^{2-}) are also easily obtained as salts. Examples are Na_2S_5, K_2S_6, and BaS_4. In addition, the S_4^{2-} and S_5^{2-} ions can serve as chelating ligands, in complexes such as $[Pt(S_5)_3]^{2-}$, whose structure is shown in Fig. 19-1. The latter is chiral and may be resolved into enantiomorphs.

19-4 Halides and Oxohalides of Sulfur

Sulfur Fluorides

Direct fluorination of S_8 yields mainly SF_6 and traces of S_2F_{10} and SF_4. The *tetrafluoride,* SF_4 (bp −30 °C), is evolved as a gas when SCl_2 is refluxed with NaF in acetonitrile at 78–80 °C.

$$3\ SCl_2 + 4\ NaF = SF_4 + S_2Cl_2 + 4\ NaCl \qquad (19\text{-}4.1)$$

SF_4 is extremely reactive, and instantly hydrolyzed by water to SO_2 and HF. It is a very selective fluorinating agent converting C═O and P═O groups smoothly into CF_2 and PF_2, and CO_2H and P(O)OH groups into CF_3 and PF_3 groups.

Sulfur hexafluoride is very resistant to chemical attack. Because of its inertness, high dielectric strength, and molecular weight, it is used as a gaseous insulator in high-voltage generators and other electrical equipment. The low reactivity is presumably due to a combination of factors including high S—F bond strength, coordinative saturation, and steric hindrance at sulfur. The inertness of SF_6 is due to kinetic factors and not to thermodynamic stability, since its reaction with H_2O to give SO_3 and HF would be decidedly favorable ($\Delta G = -460\ kJ\ mol^{-1}$).

Sulfur Chlorides

The chlorination of molten sulfur gives S_2Cl_2, which is an orange liquid of revolting smell. By using an excess of Cl_2, with traces of $FeCl_3$ or I_2 as catalyst, at room temperature, an equilibrium mixture of SCl_2 (~ 85%) and S_2Cl_2 is obtained. The dichloride (SCl_2) readily loses chlorine within a few hours, as in the equilibrium of Reaction 19-4.2,

$$2\ SCl_2 = S_2Cl_2 + Cl_2 \qquad (19\text{-}4.2)$$

but it can be obtained pure as a dark red liquid by fractional distillation in the presence of PCl_5, which stabilizes SCl_2.

Sulfur chlorides are solvents for sulfur, giving dichlorosulfanes up to about $S_{100}Cl_2$. These compounds are used in the vulcanization of rubber and are also useful as mild chlorinating agents.

Thionyl chloride ($SOCl_2$) is obtained by Reaction 19-4.3.

$$SO_2 + PCl_5 \longrightarrow SOCl_2 + POCl_3 \qquad (19\text{-}4.3)$$

It is a colorless fuming liquid (bp 80 °C) that is readily hydrolyzed as in Reaction 19-4.4.

$$SOCl_2 + H_2O \longrightarrow SO_2 + 2\ HCl \qquad (19\text{-}4.4)$$

Because the products of reactions such as 19-4.4 are volatile (and therefore easily removed), thionyl chloride is often used to prepare anhydrous chlorides, such as iron(III) chloride, as in Reactions 19-4.5 and 19-4.6.

$$Fe(OH)_3 + 3\ SOCl_2 \longrightarrow 3\ SO_2 + 3\ HCl + FeCl_3 \qquad (19\text{-}4.5)$$

$$FeCl_3 \cdot 6\ H_2O + 6\ SOCl_2 \longrightarrow 6\ SO_2 + 12\ HCl + FeCl_3 \qquad (19\text{-}4.6)$$

Thionyl chloride has a pyramidal structure with sulfur at the apex. Sulfur can be considered to be sp^3 hybridized, and it should be classified as an AB_3E system. The presence of one lone pair on sulfur allows thionyl chloride to act as a weak Lewis base. Some $d\pi$–$p\pi$ bonding between S and O is present.

Sulfuryl chloride (SO_2Cl_2) is obtained by Reaction 19-4.7.

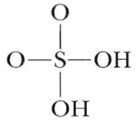
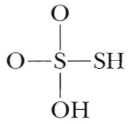
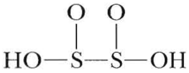
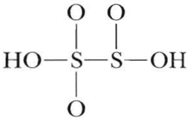
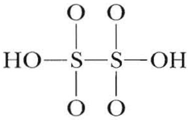
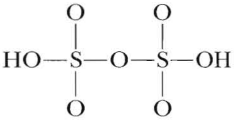
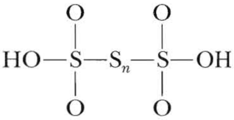
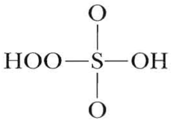
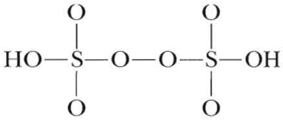
$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2 \qquad (19\text{-}4.7)$$

The reaction requires a catalyst such as $FeCl_3$. Sulfuryl chloride is a colorless liquid that fumes in moist air, due to hydrolysis. It finds use as a chlorinating agent for organic compounds. The structure of sulfuryl chloride may be considered to be derived from a tetrahedron.

19-5 Oxides and Oxo Acids

Table 19-1 lists the formulas and structures of the principal oxo acids of sulfur. In each case the sulfur may be considered to be roughly sp^3 hybridized and falls

Table 19-1 The Principal Oxo Acids of Sulfur

Name	Formula	Structure[a]
	Acids Containing One Sulfur Atom	
Sulfurous[b]	H_2SO_3	SO_3^{2-} (in sulfites)
Sulfuric	H_2SO_4	 $O-\overset{O}{\underset{OH}{S}}-OH$
	Acids Containing Two Sulfur Atoms	
Thiosulfuric	$H_2S_2O_3$	 $O-\overset{O}{\underset{OH}{S}}-SH$
Dithionous[c]	$H_2S_2O_4$	 $HO-\overset{O}{S}-\overset{O}{S}-OH$
Disulfurous[c]	$H_2S_2O_5$	 $HO-\overset{O}{\underset{O}{S}}-\overset{O}{S}-OH$
Dithionic	$H_2S_2O_6$	 $HO-\overset{O}{\underset{O}{S}}-\overset{O}{\underset{O}{S}}-OH$
Disulfuric	$H_2S_2O_7$	 $HO-\overset{O}{\underset{O}{S}}-O-\overset{O}{\underset{O}{S}}-OH$
	Acids Containing Three or More Sulfur Atoms	
Polythionic	$H_2S_{n+2}O_6$	 $HO-\overset{O}{\underset{O}{S}}-S_n-\overset{O}{\underset{O}{S}}-OH$
	Peroxo Acids	
Peroxomonosulfuric	H_2SO_5	 $HOO-\overset{O}{\underset{O}{S}}-OH$
Peroxodisulfuric	$H_2S_2O_8$	 $HO-\overset{O}{\underset{O}{S}}-O-O-\overset{O}{\underset{O}{S}}-OH$

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[a] In most cases the structure given is inferred from the structure of anions in salts of the acid.

[b] The acid is stable in the gas phase as $(HO)_2S{=}O$.

[c] The free acid is unknown.

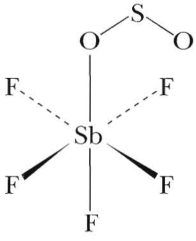
into either classification AB_3E or AB_4. Extensive $d\pi$–$p\pi$ bonding between oxygen and sulfur is to be expected. We approach the chemistry of the acids by considering that they are derived from hydration of the acidic anhydrides SO_2 or SO_3, or by protonation of the corresponding anions (e.g., sulfates or sulfites).

The Dioxides

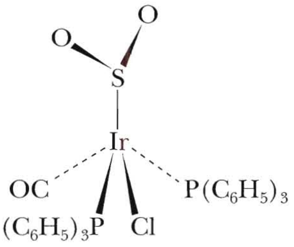
The *dioxides* are obtained by burning the elements in air. Sulfur dioxide is produced when many sulfides are heated in air. Selenium and tellurium dioxides are also obtained by treating the elements with hot nitric acid to form H_2SeO_3 and 2 $TeO_2 \cdot HNO_3$, respectively, and then heating these to drive off water or nitric acid.

Sulfur dioxide is a gas with a pungent smell. The molecule is angular. Liquid SO_2 (bp −10 °C) dissolves many organic and inorganic substances and is used as a solvent for NMR studies, as well as in preparative reactions. The liquid does not undergo self-ionization, and any conductivity it may display is due to impurities.

Sulfur dioxide has lone pairs and can act as a Lewis base. However, it also acts as a Lewis acid giving complexes, for example, with amines, as in $(CH_3)_3NSO_2$ and with electron-rich transition metal complexes. In the crystalline compound $SbF_5 \cdot SO_2$, which is of interest because of the use of SO_2 as a solvent for super-acid systems (Section 7-13), the SO_2 is bound as in Structure 19-III. The bonding in Structure 19-IV differs in that the S atom is bound to the metal.



19-III



19-IV

Metal–sulfur bonding appears to be general in transition metal species. Sulfur dioxide also undergoes "insertion" reactions (Chapter 30) with metal–carbon bonds, for example,

$$RCH_2HgOAc + SO_2 \longrightarrow RCH_2SO_2HgOAc \tag{19-5.1}$$

$$(CH_3)_4Sn + SO_2 \longrightarrow (CH_3)_3SnSO_2CH_3 \tag{19-5.2}$$

Sulfur dioxide is quite soluble in water; such solutions, which possess acidic properties, have long been referred to as solutions of *sulfurous acid*, H_2SO_3. However, H_2SO_3 is either not present or present only in infinitesimal quantities in such solutions. The so-called hydrate, $H_2SO_3 \cdot {\sim}6H_2O$, is the gas hydrate (Section 9-5), $SO_2 \cdot {\sim}7H_2O$. The equilibria in aqueous solutions of SO_2 are best represented as

$$SO_2 + x\,H_2O = SO_2 \cdot x\,H_2O \quad \text{(hydrated } SO_2\text{)} \tag{19-5.3}$$

$$[SO_2 \cdot x\,H_2O = H_2SO_3 \quad K \ll 1] \tag{19-5.4}$$

$$SO_2 \cdot x\,H_2O = HSO_3^-(aq) + H_3O^+ + (x-2)H_2O \tag{19-5.5}$$

and the first acid dissociation constant for "sulfurous acid" is properly defined as follows:

$$K_1 = \frac{[HSO_3^-][H^+]}{[\text{Total dissolved } SO_2] - [HSO_3^-] - [SO_3^{2-}]} = 1.3 \times 10^{-2}$$

Although sulfurous acid does not exist, two series of salts, the *bisulfites* (containing HSO_3^-) and the *sulfites* (containing SO_3^{2-}) are well known. The SO_3^{2-} ion in crystals is pyramidal. Only the water-soluble alkali sulfites and bisulfites are commonly encountered.

Heating solid bisulfites or passing SO_2 into their aqueous solutions affords *pyrosulfites*.

$$2\ MHSO_3 \overset{\text{heat}}{\rightleftharpoons} M_2S_2O_5 + H_2O$$

$$HSO_3^-(aq) + SO_2 = HS_2O_5^-(aq)$$

Whereas pyro acids, e.g., pyrosulfuric, $H_2S_2O_7$, (Section 7-11) usually have oxygen bridges, the pyrosulfite ion has an unsymmetrical structure, $O_2S—SO_3$. Some important reactions of sulfites are shown in Fig. 19-2.

Solutions of SO_2 and of sulfites possess reducing properties and are often used as reducing agents.

$$SO_4^{2-} + 4\ H^+ + (x-2)H_2O + 2\ e^- = SO_2 \cdot x\ H_2O \qquad E^\circ = 0.17\ V \tag{19-5.9}$$

$$SO_4^{2-} + H_2O + 2\ e^- = SO_3^{2-} + 2\ OH^- \qquad E^\circ = -0.93\ V \tag{19-5.10}$$

Selenium dioxide is a white volatile solid; the gas consists of discrete and symmetrically bent molecules very similar to those of SO_2. In the solid state, the molecules of SeO_2 associate through O→Se donor bonds. For TeO_2, this type of association through adduct formation is so strong that the compound is not volatile.

The Trioxides

Sulfur trioxide is obtained by reaction of SO_2 with O_2, a reaction that is thermodynamically very favorable but extremely slow in the absence of a catalyst such as platinum sponge, V_2O_5, or NO. Sulfur trioxide reacts vigorously with water to form sulfuric acid. Industrially, SO_3 is absorbed in concentrated H_2SO_4 to give oleum (Section 7-11), which is then diluted. Sulfur trioxide is used as such for

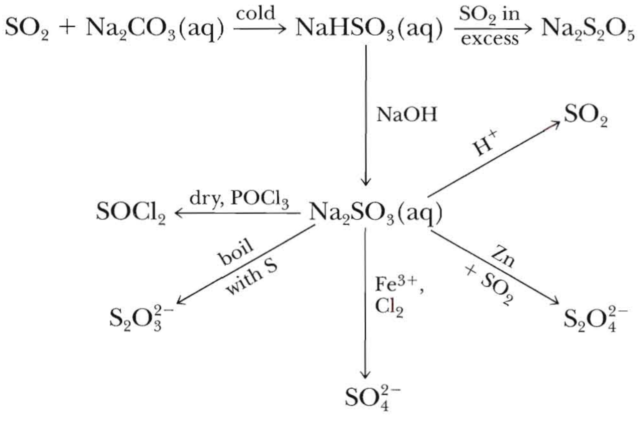


Figure 19-2 Some reactions of sulfites.

preparing sulfonated oils and alkyl arenesulfonate detergents. It is also a powerful, but generally indiscriminate, oxidizing agent.

The SO_3 molecule, in the gas phase, has a planar, triangular structure involving both $p\pi$–$p\pi$ and $p\pi$–$d\pi$ S—O bonding and forms polymers in the solid state.

Sulfuric, Selenic, and Telluric Acids

Sulfuric acid has already been discussed in Chapter 7. *Selenic acid* is similar to H_2SO_4, including the isomorphism of the hydrates and salts. It differs in being less stable, evolving oxygen above 200 °C, and being a strong but usually not kinetically fast oxidizing agent.

$$SeO_4^{2-} + 4\ H^+ + 2\ e^- = H_2SeO_3 + H_2O \quad E° = 1.15\ V \qquad (19\text{-}5.11)$$

Telluric acid, which is obtained by oxidation of Te or TeO_2 with H_2O_2 or other powerful oxidants, is very different in structure, being $Te(OH)_6$ in the crystalline form. It is a very weak dibasic acid ($K_1 \approx 10^{-7}$) and is also an oxidant. Most tellurates contain TeO_6 octahedra as in $K[TeO(OH)_5$ or Hg_3TeO_6.

Thiosulfates

Thiosulfates are readily obtained by boiling solutions of sulfites with sulfur. The acid is unstable in aqueous solution. The alkali thiosulfates are manufactured for use in photography, where they are used to dissolve unreacted silver bromide from emulsions, by formation of the complexes $[AgS_2O_3]^-$ and $[Ag(S_2O_3)_2]^{3-}$; the thiosulfate ion also forms complexes with other metal ions.

The thiosulfate ion has the structure $S—SO_3^{2-}$, Structure 19-V:

S—S = 2.01 Å

S—O = 1.47 Å

19-V

and may be considered to be derived from sulfate by replacement of an O atom by a S atom.

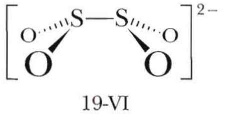
Dithionites

The reduction of sulfites in aqueous solutions containing an excess of SO_2, by zinc dust, gives ZnS_2O_4. The Zn^{2+} and Na^+ salts are commonly used as powerful and rapid reducing agents in alkaline solution.

$$2\ SO_3^{2-} + 2\ H_2O + 2\ e^- = 4\ HO^- + S_2O_4^{2-} \quad E° = -1.12\ V \qquad (19\text{-}5.12)$$

In the presence of 2-anthraquinonesulfonate as a catalyst, aqueous $Na_2S_2O_4$ efficiently removes oxygen from inert gases.

The dithionite ion has the structure $O_2S—SO_2^{2-}$, shown in Structure 19-VI:



S—S = 2.39 Å

S—O = 1.51 Å

19-VI

The eclipsed conformation, shown in Structure 19-VI, is found only in salts with small cations, whereas in solution it has the staggered conformation. The S—S bond is long and weak.

Dithionates

The dithionate ion has the staggered structure $O_3S—SO_3^{2-}$. The ion is usually obtained by oxidation of sulfite or SO_2 solutions with manganese(IV) oxide as in Reaction 19-5.13.

$$MnO_2 + 2\ SO_3^{2-} + 4\ H^+ \longrightarrow Mn^{2+} + S_2O_6^{2-} + 2\ H_2O \qquad (19\text{-}5.13)$$

The ion itself is stable and solutions of its salts may be boiled without decomposition. It resists reaction with most oxidizing and reducing agents and is therefore a useful counterion for precipitating complex cations. The free acid may be obtained by treatment of the anion in aqueous solution with sulfuric acid. Dithionic acid is a moderately strong acid that decomposes slowly in concentrated solution or when warmed. Other salts of dithionate (e.g., BaS_2O_6) may be obtained by titration of an aqueous solution of the acid with the appropriate base [e.g., $Ba(OH)_2$]. Such salts are frequently hydrated, barium dithionate being obtained as the dihydrate, $BaS_2O_6 \cdot 2H_2O$.

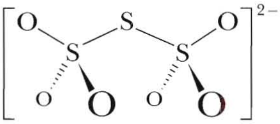
Polythionates

Polythionate anions have the general formula $[O_3SS_nSO_3]^{2-}$. The corresponding acids are not stable, decomposing rapidly into S, SO_2, and sometimes SO_4^{2-}. The well-established polythionate anions are those with $n = 1$–4. They are named according to the total number of sulfur atoms and are thus called: trithionate ($S_3O_6^{2-}$), tetrathionate ($S_4O_6^{2-}$), and so on. There is evidence for anions having chains with up to 20 sulfur atoms.

Tetrathionates are obtained by treatment of thiosulfates with iodine in the reaction used in the volumetric determination of iodine.

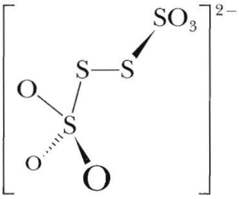
$$2\ S_2O_3^{2-} + I_2 \longrightarrow 2\ I^- + S_4O_6^{2-} \qquad (19\text{-}5.14)$$

The structures of trithionate and tetrathionate are shown in Structures 19-VII and 19-VIII, respectively.



19-VII

S—S = 2.15 Å



19-VIII

OS—S = 2.12 Å

SS—S = 2.02 Å

Peroxodisulfates

The NH_4^+ or Na^+ salts are obtained by electrolysis of the corresponding sulfates at low temperatures and high current densities. The $S_2O_8^{2-}$ ion has the structure $O_3S—O—O—SO_3$, with approximately tetrahedral angles about each S atom.

The ion is one of the most powerful and useful of oxidizing agents.

$$S_2O_8^{2-} + 2\ e^- = 2\ SO_4^{2-} \qquad E^\circ = 2.01\ V \qquad (19\text{-}5.15)$$

However, the reactions are complicated mechanistically. Oxidations by $S_2O_8^{2-}$ are slow and are usually catalyzed by addition of Ag^+, which is converted to Ag^{2+}, the actual oxidant.

STUDY GUIDE

Study Questions

A. Review

1. What are the principal forms in which sulfur occurs in nature?
2. Ordinary solid sulfur consists of what species? Summarize briefly what is observed when sulfur is heated from below its melting point to above its boiling point and explain the reasons for these changes.
3. What types of species are formed on dissolving S, Se, and Te in oleums or other superacids?
4. Discuss the aqueous chemistry of H_2S, SH^-, and S^{2-}.
5. What are the principal fluorides of sulfur?
6. Write equations for the preparations and for the reactions with water of thionyl chloride and sulfuryl chloride.
7. Write equations for the two most important reactions, or types of reaction, of SO_3.
8. Of what use(s) is SO_2?
9. Mention the chief similarities and differences among sulfuric, selenic, and telluric acids.
10. Give general formulas for three series of compounds that contain chains of more than two S atoms.

B. Additional Exercises

1. Compare the boiling points and the acid strengths in the series H_2X, where X = O through Te. Explain the trends.
2. Although SF_6 is unreactive, TeF_6 is hydrolyzed by water. Explain.
3. Describe the preparation and uses of SF_4 and SF_6.
4. Why is it that $SOCl_2$ can act both as a Lewis acid and as a Lewis base?
5. Predict the structure and describe the bonding in $SeOCl_2(py)_2$.
6. Unlike SO_2, SeO_2 is a solid with a chain structure. Draw a reasonable Lewis diagram for such a structure.
7. Draw Lewis diagrams for the following molecules and ions, giving the AB_xE_y classification, the hybridization, and the geometry at each sulfur atom:

   (a) $S_2O_3^{2-}$ (b) $S_2O_4^{2-}$

(c) $S_2O_6^{2-}$ (d) SO_2
(e) SO_3 (f) $SOCl_2$
(g) SO_2Cl_2 (h) SCl_2
(i) S_2Cl_2

8. The bond order of the S—O bond decreases in the series $OSF_2 > OSCl_2 > OSBr_2$. Explain.

9. Predict the structure of the adduct between $SbCl_5$ and $OPCl_3$.

10. Write a balanced equation for the dehydration of selenous acid.

11. Draw pictures representing the orbitals as they overlap in forming $p\pi$–$d\pi$ bonds in SO_3.

12. Prepare an MO energy-level diagram for the π-bond system in SO_3. Use the group orbital approach as described in Chapter 3, and construct π-molecular orbitals centered on the *d* atomic orbitals of S.

13. The S—O bond length in SO_4^{2-} is 1.44 Å and the S—O bond length in SO_3 is 1.42 Å. Compare these with the bond lengths given in the chapter for $S_2O_3^{2-}$, $S_2O_4^{2-}$, $S_3O_6^{2-}$, and $S_4O_6^{2-}$, and with the sum (S + S and S + O) of the S—S and the S—O covalent single-bond radii. Discuss the relative strengths of S—O and S—S bonds in these systems.

C. Questions from the Literature of Inorganic Chemistry

1. Consider the oxofluorides of Se and Te as reported by H. Oberhammer and K. Seppelt, *Inorg. Chem.*, **1979,** *18,* 2226–2229.

(a) Draw the Lewis diagrams and discuss the hybridization and geometry (using the AB_xE_y classification and the VSEPR approach) of the following oxofluorides mentioned in this paper: SeO_2F_2, $SeOF_4$, $Se_2O_2F_8$, $Te_2O_2F_8$, $I_2O_4F_6$, F_5SOSF_5, and $F_5SeOSeF_5$.

(b) In which compounds in (a) is $d\pi$–$p\pi$ bonding between O and Se (or Te) important? Explain.

(c) What reason(s) do the authors give for the tendency of $SeOF_4$ to dimerize giving $Se_2O_2F_8$? Explain.

(d) Do you suppose $TeOF_4$ is stable? Explain.

2. Consider the adducts of SO_2 described by P. G. Eller and G. J. Kubas, *Inorg. Chem.*, **1978,** *17,* 894–897.

(a) Does SO_2 serve as a Lewis acid or as a Lewis base in forming ISO_2^-?

(b) Other adducts XSO_2^- were not isolated, but stabilities of the adducts were studied. How?

(c) Draw the Lewis diagram for ISO_2^- and discuss the structural data presented in the article. Classify the S atom according to the AB_xE_y system.

(d) What is the significance of the I—S distance found in this study? Compare this I—S distance with the sum $r_{cov}(I + S)$ and the sum $r_{vdw}(I + S)$. Is this a fully covalent I—S bond?

3. Consider the paper by C. J. Schack, R. D. Wilson, and J. F. Hon, *Inorg. Chem.*, **1972,** *11,* 208-209.

(a) Write balanced equations for every step in each synthesis of SeF_5Cl as reported in this paper.

(b) What is the equation representing the hydrolysis in aqueous hydroxide solution of SeF_5Cl? How was this hydrolysis used to analyze the compound?

(c) With what other compounds of S and Se do the authors suggest a similarity? On what basis are these comparisons made?

SUPPLEMENTARY READING

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