

Mixed complexes in which a metal is coordinated by a dithiolene and by other ligands such as ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>), CO, NO, R<sub>3</sub>P, etc., are also known.

## 15.2 Compounds of Sulfur

### 15.2.1 Sulfides of the metallic elements<sup>(98,99)</sup>

Many of the most important naturally occurring minerals and ores of the metallic elements are sulfides (p. 648), and the recovery of metals from these ores is of major importance. Other metal sulfides, though they do not occur in nature, can be synthesized by a variety of preparative methods, and many have important physical or chemical properties which have led to their industrial production. Again, the solubility relations of metal sulfides in aqueous solution form the basis of the most widely used scheme of elementary qualitative analysis. These various more general considerations will be briefly discussed before the systematic structural chemistry of metal sulfides is summarized.

#### General considerations

When sulfide ores are roasted in air two possible reactions may occur:

- (a) conversion of the material to the oxide (as a preliminary to metal extraction, e.g. lead sulfide roasting);
- (b) formation of water-soluble sulfates which can then be used in hydrometallurgical processes.

The operating conditions (temperature, oxygen pressure, etc.) required to achieve each of these results depend on the thermodynamics of the

system and the duration of the roast is determined by the kinetics of the gas–solid reactions.<sup>(100)</sup> According to the Gibbs' phase rule:

$$F + P = C + 2$$

where  $F$  is the number of degrees of freedom (pressure, temperature, etc.),  $P$  is the number of phases in equilibrium and  $C$  is the number of components (independently variable chemical entities) in the system. It follows that, for a 3-component system (metal-sulfur-oxygen) at a given temperature and total pressure of the gas phase, a maximum of *three* condensed phases can coexist in equilibrium. The ranges of stability of the various solid phases at a fixed temperature can be shown on a stability diagram which plots the equilibrium pressure of SO<sub>2</sub> against the pressure of oxygen on a log–log graph. An idealized stability diagram for a divalent metal  $M$  is shown in Fig. 15.17a, and actual stability diagrams for copper at 950 K and lead at 1175 K are in Fig. 15.17b, and c. Note that, ideally, all boundaries are straight lines: those between  $M/MO$  and  $MS/MSO_4$  are vertical whereas the others have slopes of 1.0 ( $M/MS$ ), 1.5 ( $MS/MO$ ), and  $-0.5$  ( $MO/MSO_4$ ).<sup>†</sup>

The application of these generalizations to the extractive metallurgy of individual metals is illustrated at appropriate points in the text dealing with the chemistry of the various elements.

<sup>100</sup> C. B. ALCOCK, *Principles of Pyrometallurgy*, Chap. 2, pp. 15 ff., Academic Press, London, 1967.

<sup>†</sup> These simple relations can readily be deduced from the equilibria being represented. Thus at constant temperature:

$M/MO$  boundary:  $MO = M + \frac{1}{2}O_2(g)$ ;  $K = p^{1/2}(O_2)$ .  
Hence  $\log p(O_2) = 2 \log K = \text{constant}$  [i.e. independent of  $p(SO_2)$ ].

$MS/MSO_4$  boundary:  $MSO_4 = MS + 2O_2(g)$ ;  
 $K = p^2(O_2)$ . Hence  $\log p(O_2) = \frac{1}{2} \log K = \text{constant}$ .

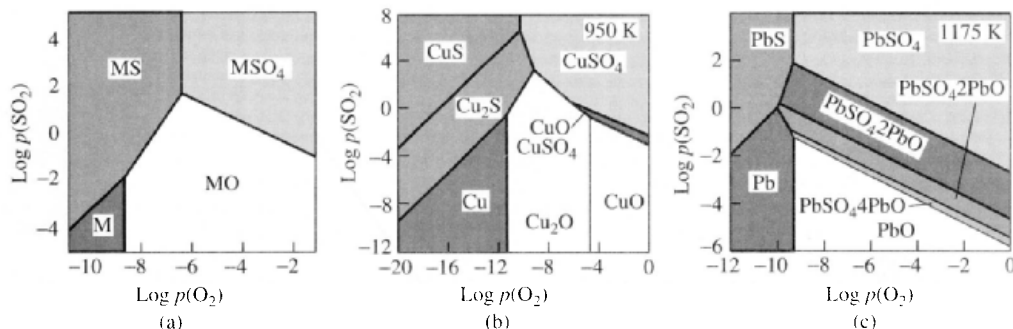
$M/MS$  boundary:  $MS + O_2(g) = M + SO_2(g)$ ;  
 $K = p(SO_2)/p(O_2)$ . Hence  $\log p(SO_2) = \log K + \log p(O_2)$ , i.e. slope = 1.0.

$MS/MO$  boundary:  $MS + \frac{3}{2}O_2(g) = MO + SO_2(g)$ ;  $K = p(SO_2)/p^{3/2}(O_2)$ . Hence  $\log p(SO_2) = \log K + \frac{3}{2} \log p(O_2)$ , i.e. slope = 1.5.

$MO/MSO_4$  boundary:  $MSO_4 = MO + SO_2(g) + \frac{1}{2}O_2(g)$ ;  
 $K = p(SO_2) \cdot p^{1/2}(O_2)$ . Hence  $\log p(SO_2) = \log K - \frac{1}{2} \log p(O_2)$ , i.e. slope =  $-0.5$ .

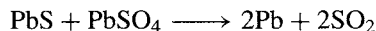
<sup>98</sup> F. JELLINEK, Sulfides, Chap. 19 in G. NICKLESS (ed.), *Inorganic Sulfur Chemistry*, pp. 669–747, Elsevier, Amsterdam, 1968. A comprehensive review with 631 references.

<sup>99</sup> D. J. VAUGHAN and J. R. CRAIG, *Mineral Chemistry of Metal Sulfides*, Cambridge University Press, Cambridge, 1978, 493 pp. A comprehensive account of the structure bonding and properties of mineral sulfides.

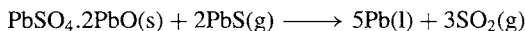


**Figure 15.17** Stability diagrams for the systems (a) metal (M)–sulfur–oxygen (idealized), (b) Cu–S–O and (c) Pb–S–O.

As noted above, the roasting of most metal sulfides yields either the oxide or sulfate. However, a few metals can be obtained directly by oxidation of their sulfides, and these all have the characteristic property that their oxides are much less stable than  $\text{SO}_2$ . Examples are Cu, Ag, Hg and the platinum metals. In addition, metallic Pb can be extracted by partial oxidation of galena to form a sulfate (the “Scotch hearth” or Newnham process, p. 370). The oversimplified reaction is:



However, as indicated in Fig. 15.17c, the system is complicated by the presence of several stable “basic sulfates”  $\text{PbSO}_4 \cdot n\text{PbO}$  ( $n = 1, 2, 4$ ), and these can react with gaseous PbS at lower metal-making temperatures, e.g.:



Metal sulfides can be prepared in the laboratory or on an industrial scale by a number of reactions; pure products are rarely obtained without considerable refinement and nonstoichiometric phases abound (p. 679). The more important preparative routes include:

- direct combination of the elements (e.g.  $\text{Fe} + \text{S} \longrightarrow \text{FeS}$ );
- reduction of a sulfate with carbon (e.g.  $\text{Na}_2\text{SO}_4 + 4\text{C} \longrightarrow \text{Na}_2\text{S} + 4\text{CO}$ );
- precipitation from aqueous solution by treatment with either acidified  $\text{H}_2\text{S}$  (e.g. the platinum metals; Cu, Ag, Au; Cd, Hg;

- Ge, Sn, Pb; As, Sb, Bi; Se, Te) or alkaline ( $\text{NH}_4$ )<sub>2</sub>S (e.g. Mn, Fe, Co, Ni, Zn; In, Tl);
- (d) saturation of an alkali hydroxide solution with  $\text{H}_2\text{S}$  to give MHS followed by reaction with a further equivalent of alkali (e.g.  $\text{KOH}(aq) + \text{H}_2\text{S} \longrightarrow \text{KHS} + \text{H}_2\text{O}$ ;  $\text{KHS} + \text{KOH} \longrightarrow \text{K}_2\text{S} + \text{H}_2\text{O}$ ).

This last method is particularly suitable for water-soluble sulfides, though frequently it is the hydrate that crystallizes, e.g.  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ,  $\text{K}_2\text{S} \cdot 5\text{H}_2\text{O}$ . The hydrosulfides MHS can also be made by passing  $\text{H}_2\text{S}$  into solutions of metals in liquid  $\text{NH}_3$ . The colourless hygroscopic mixed metal sulfide  $\text{RbKS}$  was recently made by annealing a mixture of  $\text{K}_2\text{S}$  and  $\text{Rb}_2\text{S}$ .<sup>(100a)</sup>

Industrial applications of metal sulfides span the full time-scale from the earliest rise of the emerging chemical industry in the eighteenth century to the most recent developments of Li/S and Na/S power battery systems (see Panel). Reduction of  $\text{Na}_2\text{SO}_4$  by C was the first step in the now defunct Leblanc process (1791) for making  $\text{Na}_2\text{CO}_3$  (p. 71).  $\text{Na}_2\text{S}$  (or NaHS) is still used extensively in the leather industry for removal of hair from hides prior to tanning, for making organo-sulfur dyes, as a reducing agent for organic nitro compounds in the production of amines, and as a flotation agent for copper ores. It is readily oxidized by atmospheric  $\text{O}_2$  to give

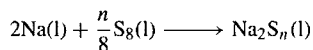
<sup>100a</sup> H. SABROWSKY and P. VOGT, *Z. anorg. allg. Chem.*, **616**, 183–5 (1992).

## Sodium-Sulfur Batteries

Alternatives to coal and hydrocarbon fuels as a source of power have been sought with increasing determination over the past three decades. One possibility is the Hydrogen Economy (p. 40). Another possibility, particularly for secondary, mobile sources of power, is the use of storage batteries. Indeed, electric vehicles were developed simultaneously with the first internal-combustion-engined vehicles, the first being made in 1888. In those days, over a century ago, electric vehicles were popular and sold well compared with the then noisy, inconvenient and rather unreliable petrol-engined vehicles. In 1899 an electric car held the world land-speed record at 105 km per hour. In the early years of this century, taxis in New York, Boston and Berlin were mainly electric; there were over 20000 electric vehicles in the USA and some 10000 cars and commercial vehicles in London. Even today (silent) battery-powered milk delivery vehicles are still operated in the UK. These use the traditional lead-sulfuric acid battery (p. 371), but this is extremely heavy and rather expensive.

The Na/S system has the potential to store 5-times as much energy (for the same weight) as the conventional lead battery and, in addition, shares with it the advantages of being silent, cheap to run, and essentially pollution-free: in general it is also reliable, has a long life and has extremely low maintenance costs. However, until recently it lacked the mileage range between successive chargings when compared with the highly developed petrol- or diesel-powered vehicles and it has a rather low performance (top speed and acceleration). A further disadvantage is the very long time taken to recharge the batteries (15–20 h) compared with the average time required to refill a petrol tank (1–2 min). Mixed power sources (petrol/electric battery) are a possible mode for development.

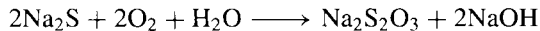
Conventional batteries consist of a liquid electrolyte separating two solid electrodes. In the Na/S battery this is inverted: a solid electrolyte separates two liquid electrodes: a ceramic tube made from the solid electrolyte sodium  $\beta$ -alumina (p. 249) separates an inner pool of molten sodium (mp 98°) from an outer bath of molten sulfur (mp 119°) and allows  $\text{Na}^+$  ions to pass through. The whole system is sealed and is encased in a stainless steel canister which also serves as the sulfur-electrode current collector. Within the battery, the current is passed by  $\text{Na}^+$  ions which pass through the solid electrolyte and react with the sulfur. The cell reaction can be written formally as



In the central compartment molten Na gives up electrons which pass through the external circuit and reduce the molten  $\text{S}_8$  to polysulfide ions  $\text{S}_n^{2-}$  (p. 681). The open circuit voltage is 2.08 V at 350°C. Since sulfur is an insulator the outer compartment is packed with porous carbon to provide efficient electrical conduction: the electrode volume is partially filled with sulfur when fully charged and is completely filled with sodium sulfide when fully discharged. To recharge, the polarity of the electrodes is changed and the passage of current forces the  $\text{Na}^+$  ions back into the central compartment where they are discharged as Na atoms.

Typical dimensions for the  $\beta$ -alumina electrolyte tube are 380 mm long, with an outer diameter of 28 mm, and a wall thickness of 1.5 mm. A typical battery for automotive power might contain 980 of such cells (20 modules each of 49 cells) and have an open-circuit voltage of 100 V. Capacity exceeds 50 kWh. The cells operate at an optimum temperature of 300–350°C (to ensure that the sodium polysulfides remain molten and that the  $\beta$ -alumina solid electrolyte has an adequate  $\text{Na}^+$  ion conductivity). This means that the cells must be thermally insulated to reduce wasteful loss of heat and to maintain the electrodes molten even when not in operation. Such a system is about one-fifth of the weight of an equivalent lead-acid traction battery and has a similar life (~1000 cycles).

thiosulfate:

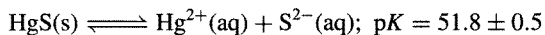


World production of  $\text{Na}_2\text{S}$  exceeds 150 000 tonnes pa and that of NaHS approaches 100 000 tpa. Barium sulfide (from  $\text{BaSO}_4 + \text{C}$ ) is the largest volume Ba compound manufactured but little of it is sold; almost all commercial Ba compounds are made by first making BaS and then converting it to the required compound.

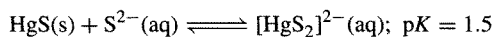
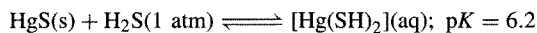
Metal sulfides vary enormously in their solubility in water. As expected, the (predominantly ionic) alkali metal sulfides and alkaline earth metal sulfides are quite soluble though there is appreciable hydrolysis which results in

strongly alkaline solutions ( $\text{M}_2\text{S} + \text{H}_2\text{O} \longrightarrow \text{MSH} + \text{MOH}$ ). Accordingly, solubilities depend sensitively not only on temperature but also on pH and partial pressure of  $\text{H}_2\text{S}$ . Thus, by varying the acidity, As can be separated from Pb, Pb from Zn, Zn from Ni, and Mn from Mg. In pure water the solubility of  $\text{Na}_2\text{S}$  is said to be 18.06 g per 100 g  $\text{H}_2\text{O}$  and for  $\text{Ba}_2\text{S}$  it is 7.28 g. In the case of some less-basic elements (e.g.  $\text{Al}_2\text{S}_3$ ,  $\text{Cr}_2\text{S}_3$ ) hydrolysis is complete and action of  $\text{H}_2\text{S}$  on solutions of the metal cation results in the precipitation of the hydroxide; likewise these sulfides (and  $\text{SiS}_2$ , etc.) react rapidly with water with evolution of  $\text{H}_2\text{S}$ .

By contrast with the water-soluble sulfides of Groups 1 and 2, the corresponding heavy metal sulfides of Groups 11 and 12 are amongst the least-soluble compounds known. Literature values are often wildly discordant, and care should be taken in interpreting the data. Thus, for black HgS the most acceptable value of the solubility product  $[\text{Hg}^{2+}][\text{S}^{2-}]$  is  $10^{-51.8} \text{ mol}^2 \text{ l}^{-2}$ , i.e.



However, this should not be taken to imply a concentration of only  $10^{-25.9} \text{ mol l}^{-1}$  for mercury in solution (i.e. less than  $10^{-2}$  of 1 atom of Hg per litre!) since complex formation can simultaneously occur to give species such as  $[\text{Hg}(\text{SH})_2]$  in weakly acid solutions and  $[\text{HgS}_2]^{2-}$  in alkaline solutions:



Hydrolysis also sometimes obtrudes.

### Structural chemistry of metal sulfides

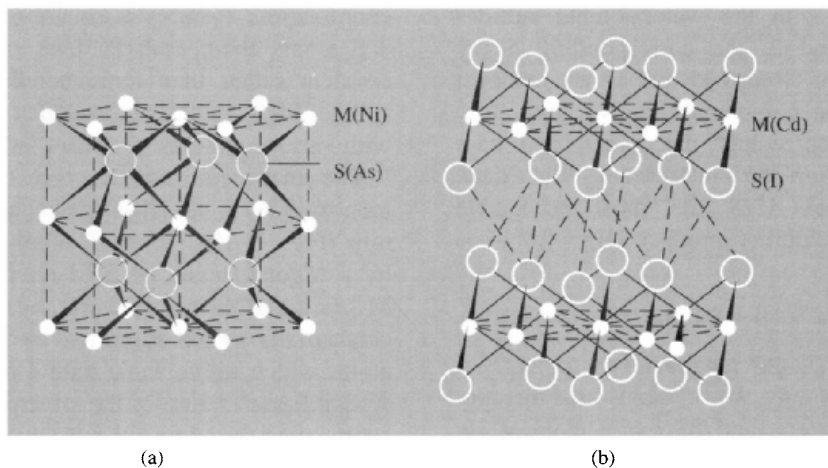
The predominantly ionic alkali metal sulfides  $\text{M}_2\text{S}$  (Li, Na, K, Rb, Cs) adopt the antifluorite structure (p. 118) in which each S atom is surrounded by a cube of 8 M and each M by a tetrahedron of S. The alkaline earth sulfides MS (Mg, Ca, Sr, Ba) adopt the NaCl-type 6:6 structure (p. 242) as do many other monosulfides of rather less basic metals ( $\text{M} = \text{Pb}, \text{Mn}, \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Tb}, \text{Ho}, \text{Th}, \text{U}, \text{Pu}$ ). However, many metals in the later transition element groups show substantial trends to increasing covalency leading either to lower coordination numbers or to layer-lattice structures.<sup>(101)</sup> Thus MS (Be, Zn, Cd, Hg) adopt the 4:4 zinc blende structure (p. 1210) and ZnS, CdS and MnS also crystallize in the 4:4 wurtzite modification (p. 1210). In both of these structures both M and S are tetrahedrally coordinated, whereas PtS, which also has 4:4

coordination, features a square-planar array of 4 S atoms about each Pt, thus emphasizing its covalent rather than ionic bonding. Group 13 sulfides  $\text{M}_2\text{S}_3$  (p. 252) have defect ZnS structures with various patterns of vacant lattice sites.

The final major structure type found amongst monosulfides is the NiAs (nickel arsenide) structure (Fig. 15.18a). Each S atom is surrounded by a trigonal prism of 6 M atoms whilst each M has eightfold coordination, being surrounded octahedrally by 6 S atoms and by 2 additional M atoms which are coplanar with 4 of the S atoms. A significant feature of the structure is the close approach of the M atoms in chains along the (vertical) *c*-axis (e.g. 260 pm in FeS) and the structure can be regarded as transitional between the 6:6 NaCl structure and the more highly coordinated structures typical of metals. The NiAs structure is adopted by most first row transition-metal monosulfides MS ( $\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Fe}, \text{Co}, \text{Ni}$ ) as well as by many selenides and tellurides of these elements.

The NiAs structure is closely related to the hexagonal layer-lattice  $\text{CdI}_2$  structure shown in Fig. 15.18b, this stoichiometry being achieved simply by leaving alternate M layers of the NiAs structure vacant. Disulfides  $\text{MS}_2$  adopting this structure include those of Ti, Zr, Hf, Ta, Pt and Sn; conversely,  $\text{Tl}_2\text{S}$  has the anti- $\text{CdI}_2$  structure. Progressive partial filling of the alternate metal layers leads to phases of intermediate composition as exemplified by the Cr/S system (Table 15.10). For some elements these intermediate phases have quite extensive ranges of composition, the limits depending on the temperature of the system. For example, at 1000°C there is a succession of non-stoichiometric titanium sulfides  $\text{TiS}_{0.97} - \text{TiS}_{1.06}$ ,  $\text{TiS}_{1.204} - \text{TiS}_{1.333}$ ,  $\text{TiS}_{1.377} - \text{TiS}_{1.594}$ ,  $\text{TiS}_{1.810} - \text{TiS}_{1.919}$ .<sup>(101)</sup> Many diselenides and ditellurides also adopt the  $\text{CdI}_2$  structure and in some there is an almost continuous nonstoichiometric variation in composition, e.g.  $\text{CoTe} \longrightarrow \text{CoTe}_2$ . A related 6:3 layer structure is the  $\text{CdCl}_2$ -type adopted by  $\text{TaS}_2$ , and the layer structures of  $\text{MoS}_2$  and  $\text{WS}_2$  are mentioned on p. 1018.

<sup>101</sup> N. N. GREENWOOD, *Ionic Crystals, Lattice Defects, and Nonstoichiometry*, Chap. 3, pp. 37-61; also pp. 153-5, Butterworths, London, 1968.



**Figure 15.18** Comparison of the nickel arsenide structure (a) adopted by many monosulfides  $MS$  with the cadmium iodide structure (b) adopted by some disulfides  $MS_2$ . The structures are related simply by removing alternate layers of  $M$  from  $MS$  to give  $MS_2$ .

**Table 15.10** Some sulfides of chromium (see text)

Nominal formula	Ratio Cr/S		Proportion of sites occupied in alternate layers	Random or ordered vacancies <sup>(a)</sup>
	calculated	observed		
$CrS^{(b)}$	1.000	$\approx 0.97$	1:1	None
$Cr_7S_8$	0.875	0.88–0.87	$1:\frac{3}{4}$	Random
$Cr_5S_6$	0.833	0.85	$1:\frac{2}{3}$	Ordered
$Cr_3S_4$	0.750	0.79–0.76	$1:\frac{1}{2}$	Ordered
$Cr_2S_3$	0.667	0.69–0.67	$1:\frac{1}{3}$	Ordered
$(CrS_2)$	0.500	Not observed	1:0	—

<sup>(a)</sup>Refers to the vacancies in the alternate metal layers.

<sup>(b)</sup> $CrS$  has a unique monoclinic structure intermediate between  $NiAs$  and  $PtS$  types.

Finally, many disulfides have a quite different structure motif, being composed of infinite three-dimensional networks of  $M$  and discrete  $S_2$  units. The predominate structural types are pyrites,  $FeS_2$  (also for  $M = Mn, Co, Ni, Ru, Os$ ), and marcasite (known only for  $FeS_2$  among the disulfides). Pyrites can be described as a distorted  $NaCl$ -type structure in which the rod-shaped  $S_2$  units ( $S-S$  217 pm) are centred on the  $Cl$  positions but are oriented so that they are inclined away from the cubic axes. The marcasite structure is a variant of the rutile structure ( $TiO_2$ ,

p. 961) in which the columns of edge-shared octahedra are rotated to give close approaches between pairs of  $S$  atoms in adjacent columns ( $S-S$  221 pm).

Many metal sulfides have important physical properties.<sup>(98,102)</sup> They range from insulators, through semiconductors to metallic conductors of electricity, and some are even superconductors,

<sup>102</sup>F. HULLIGER, *Struct. Bonding* (Berlin) **4**, 83–229 (1968). A comprehensive review with 532 references, 65 structural diagrams, and a 34-page appendix tabulating the known phases and their physical properties.

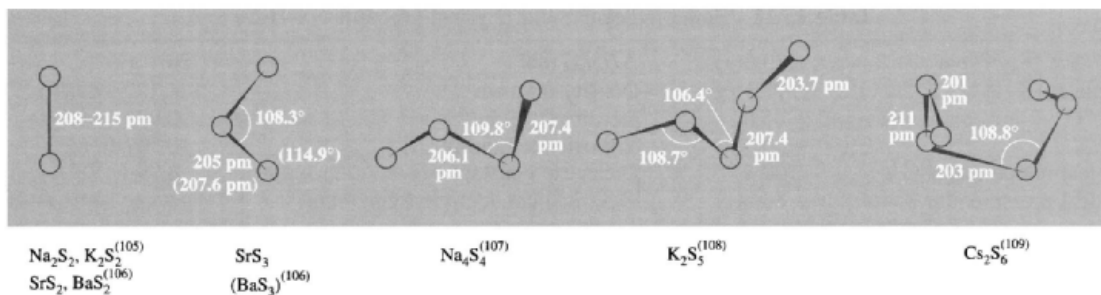


Figure 15.19 Structures of polysulfide anions  $S_n^{2-}$  in  $M_2S_n$  and  $BaS_n$ .

e.g.  $NbS_2$  (<6.2 K),  $TaS_2$  (<2.1 K),  $Rh_{17}S_{15}$  (<5.8 K),  $CuS$  (<1.62 K) and  $CuS_2$  (<1.56 K). Likewise they can be diamagnetic, paramagnetic, temperature-independent paramagnetic, ferromagnetic, antiferromagnetic or ferrimagnetic.

The structures of more complex ternary metal sulfides such as  $BaZrS_3$  (perovskite-type, p. 963),  $ZnAl_2S_4$  (spinel type, p. 247), and  $NaCrS_2$  (NaCl superstructure) introduce no new principles. Likewise, thiosalts, which may feature finite anions (e.g.  $Tl_3[VS_4]$ ), vertex-shared chains (e.g.  $Ba_2MnS_3$ ), edge-shared chains (e.g.  $KFeS_2$ ), double chains (e.g.  $Ba_2ZnS_3$ ), double layers (e.g.  $KCu_4S_3$ ) or three-dimensional frameworks (e.g.  $NH_4Cu_7S_4$ ).<sup>(103)</sup> Finite clusters also abound.<sup>(104)</sup>

### Anionic polysulfides

The pyrites and marcasite structures can be thought of as containing  $S_2^{2-}$  units though the variability of the interatomic distance and other properties suggest substantial deviation from a purely ionic description. Numerous higher polysulfides  $S_n^{2-}$  have been characterized, particularly for the more electropositive elements Na, K, Ba, etc. They are yellow at room temperature, turn dark red on being heated, and may be thought of as salts of the polysulfanes

(p. 683). Typical examples are  $M_2S_n$  ( $n = 2-5$  for Na, 2-6 for K, 6 for Cs),  $BaS_2$ ,  $BaS_3$ ,  $BaS_4$ , etc. The polysulfides, unlike the monosulfides, are low melting solids: published values for mps vary somewhat but representative values ( $^{\circ}C$ ) are:

$Na_2S$ 1180°	$Na_2S_2$ 484°	$Na_2S_4$ 294°	$Na_2S_5$ 255°	
$K_2S_3$ 292°	$K_2S_4$ ~145°	$K_2S_5$ 211°	$K_2S_6$ 196°	$BaS_3$ 554°

Structures are in Fig. 15.19. The  $S_3^{2-}$  ion is bent ( $C_{2v}$ ) and is isoelectronic with  $SCl_2$  (p. 689). The  $S_4^{2-}$  ion has twofold symmetry, essentially tetrahedral bond angles, and a dihedral angle of  $97.8^{\circ}$  (see p. 654). The  $S_5^{2-}$  ion also has approximately twofold symmetry (about the central S atom); it is a contorted but unbranched chain with bond angles close to tetrahedral and a small but significant difference between the terminal and internal S-S distances. The  $S_6^{2-}$  ion has alternating S-S distances, and bond angles in the range  $106.4-110.0^{\circ}$  (mean  $108.8^{\circ}$ ). Several of the references in Fig. 15.19 give preparative details: these can involve direct reaction of

<sup>105</sup> H. FOPPL, E. BUSMANN, and F.-K. FRORATH, *Z. anorg. allg. Chem.* **314**, 12-30 (1962).

<sup>106</sup> H. G. VON SCHNERING and N.-K. GOH, *Naturwissenschaften* **61**, 272 (1974).

<sup>107</sup> R. TEGMAN, *Acta Cryst.* **B29**, 1463-9 (1973).

<sup>108</sup> B. KELLY and P. WOODWARD, *J. Chem. Soc., Dalton Trans.*, 1314-6 (1976).

<sup>109</sup> S. C. ABRAHAMS and E. GRISON, *Acta Cryst.* **6**, 206-13 (1953).

<sup>103</sup> A. F. WELLS, *Structural Inorganic Chemistry*, 5th edn., Chap. 17 pp. 748-87, Oxford University Press, 1984.

<sup>104</sup> I. DANCE and K. FISHER, *Prog. Inorg. Chem.* **41**, 637-803 (1994). A comprehensive review with 503 references, 100 structural diagrams and 40 pages of tabulated material.

Table 15.11 Some molecular and physical properties of H<sub>2</sub>S

Distance (S–H)/pm	133.6(g)	$\Delta H_f^\circ/\text{kJ mol}^{-1}$	20.1(g)
Angle H–S–H	92.1°(g)	Density (s)/g cm <sup>-3</sup>	1.12 (–85.6°)
MP/°C	–85.6	Density (l)/g cm <sup>-3</sup>	0.993 (–85.6°)
BP/°C	–60.3	Viscosity/centipoise	0.547 (–82°)
Critical temperature/°C	100.4	Dielectric constant $\epsilon$	8.99 (–78°)
Critical pressure/atm	84	Electrical conductivity/ohm <sup>-1</sup> cm <sup>-1</sup>	$3.7 \times 10^{-11}$ (–78°)

stoichiometric amounts of the elements in sealed tubes or reaction of MSH with S in ethanol.<sup>(110)</sup>

It is interesting that, despite the unequivocal presence of the S<sub>3</sub><sup>2-</sup> ion in K<sub>2</sub>S<sub>3</sub>, BaS<sub>3</sub>, etc., a Raman spectroscopic study of molten “Na<sub>2</sub>S<sub>3</sub>” showed that the ion had disproportionated into S<sub>2</sub><sup>2-</sup> and S<sub>4</sub><sup>2-</sup>.<sup>(111)</sup>

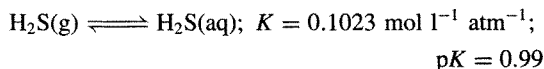
### 15.2.2 Hydrides of sulfur (sulfanes)

Hydrogen sulfide is the only thermodynamically stable sulfane; it occurs widely in nature as a result of volcanic or bacterial action and is, indeed, a prime source of elemental S (p. 647). It has been known since earliest times and its classical chemistry has been extensively studied since the seventeenth century.<sup>(112)</sup> H<sub>2</sub>S is a foul smelling, very poisonous gas familiar to all students of chemistry. Its smell is noticeable at 0.02 ppm but the gas tends to anaesthetize the olfactory senses and the intensity of the smell is therefore a dangerously unreliable guide to its concentration. H<sub>2</sub>S causes irritation at 5 ppm, headaches and nausea at 10 ppm and immediate paralysis and death at 100 ppm; it is therefore as toxic and as dangerous as HCN.

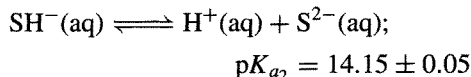
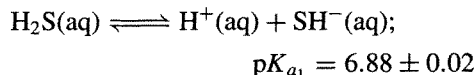
H<sub>2</sub>S is readily prepared in the laboratory by treating FeS with dilute HCl in a Kipp apparatus. Purer samples can be made by hydrolysing CaS, BaS or Al<sub>2</sub>S<sub>3</sub>, and the purest gas is prepared by direct reaction of the elements at 600°C.

Some physical properties are in Table 15.11:<sup>(113)</sup> comparison with the properties of water (p. 623) shows the absence of any appreciable H bonding in H<sub>2</sub>S.<sup>(114)</sup> Comparisons with H<sub>2</sub>Se, H<sub>2</sub>Te and H<sub>2</sub>Po are on p. 767.

H<sub>2</sub>S is readily soluble in both acidic and alkaline aqueous solutions. Pure water dissolves 4.65 volumes of the gas at 0° and 2.61 volumes at 20°; in other units a saturated solution is 0.1 M at atmospheric pressure and 25°, i.e.



In aqueous solution H<sub>2</sub>S is a weak acid (p. 49). At 20°:<sup>(115)</sup>



The chemistry of such solutions has been alluded to on p. 678. At low temperatures a hydrate H<sub>2</sub>S·5 $\frac{3}{4}$ H<sub>2</sub>O crystallizes. In acid solution H<sub>2</sub>S is also a mild reducing agent; e.g. even on standing in air solutions slowly precipitate sulfur. The gas burns with a bluish flame in air to give H<sub>2</sub>O and SO<sub>2</sub> (or H<sub>2</sub>O and S if the air supply is restricted). For adducts, see p. 673.

In very strongly acidic nonaqueous solutions (such as HF/SbF<sub>5</sub>) H<sub>2</sub>S acts as a base (proton acceptor) and the white crystalline

<sup>110</sup> G. WEDDIDEN, H. KLEINSCHMAGER and S. HOPPE, *J. Chem. Res. (S)*, 1978, 96; (*M*), 1978, 1101–12.

<sup>111</sup> G. J. JANZ *et al.*, *Inorg. Chem.* **15**, 1751–4, 1755–9, 1759–63 (1976).

<sup>112</sup> J. W. MELLOR, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 10, pp. 114–61, Longmans, London, 1930.

<sup>113</sup> F. FEHÉR, Liquid hydrogen sulfide, Chap. 4 in J. J. LAGOWSKI (ed.), *The Chemistry of Nonaqueous Solvents*, Vol. 3, pp. 219–40, Academic Press, New York, 1970.

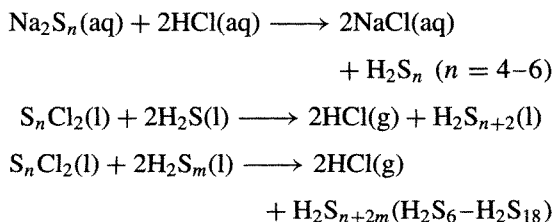
<sup>114</sup> A. N. FITCH and J. K. COCKROFT, *J. Chem. Soc., Chem. Commun.*, 515–6 (1990).

<sup>115</sup> M. WIDMER and G. SCHWARZENBACH, *Helv. Chim. Acta* **47**, 266–71 (1964).

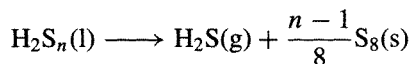
solid  $[\text{SH}_3]^+[\text{SbF}_6]^-$  has been isolated from such solutions.<sup>(116)</sup> The compound, which is the first known example of a stable salt of  $\text{SH}_3^+$ , can be stored at room temperature in Teflon or Kel-F containers but attacks quartz. Vibrational spectroscopy confirms the pyramidal  $C_{3v}$  structure expected for a species isoelectronic with  $\text{PH}_3$  (p. 492). In the presence of an excess of  $\text{H}_2\text{S}$  at  $-80^\circ\text{C}$ , the trimercaptosulfonium salts  $[\text{S}(\text{SH})_3]^+\text{AsF}_6^-$  and  $[\text{S}(\text{SH})_3]^+\text{SbCl}_6^-$  can be prepared;<sup>(117)</sup> the cation is isoelectronic with  $\text{P}(\text{PH}_2)_3$  (p. 495) and is expected to have  $C_{3v}$  symmetry.

Polysulfanes,  $\text{H}_2\text{S}_n$ , with  $n = 2-8$  have been prepared and isolated pure, and many higher homologues have been obtained as mixtures with variable  $n$ . Our modern knowledge of these numerous compounds stems mainly from the elegant work of F. Fehér and his group in the 1950s. All polysulfanes have unbranched chains of  $n$  sulfur atoms thus reflecting the well-established propensity of this element towards catenation (p. 652). The polysulfanes are reactive liquids whose density  $d$ , viscosity  $\eta$ , and bp increase with increasing chain length.  $\text{H}_2\text{S}_2$ , the analogue of  $\text{H}_2\text{O}_2$ , is colourless but the others are yellow, the colour deepening with increasing chain length.

The polysulfanes were at one time made by fusing crude  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  with various amounts of sulfur and pouring the resulting polysulfide solution into an excess of dilute hydrochloric acid at  $-10^\circ\text{C}$ . The resulting crude yellow oil is a mixture mainly of  $\text{H}_2\text{S}_n$  ( $n = 4-7$ ). Polysulfanes can now also be readily prepared by a variety of other reactions, e.g.:



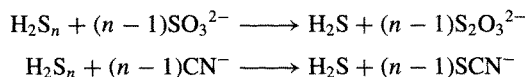
Purification is by low-pressure distillation. Some physical properties are in Table 15.12. Polysulfanes are readily oxidized and all are thermodynamically unstable with respect to disproportionation:



**Table 15.12** Some physical properties of polysulfanes<sup>(118)</sup>

Compound	$d_{20}/\text{g cm}^{-3}$	$P_{20}/\text{mmHg}$	BP/ $^\circ\text{C}$ (extrap)
$\text{H}_2\text{S}_2$	1.334	87.7	70
$\text{H}_2\text{S}_3$	1.491	1.4	170
$\text{H}_2\text{S}_4$	1.582	0.035	240
$\text{H}_2\text{S}_5$	1.644	0.0012	285
$\text{H}_2\text{S}_6$	1.688	—	—
$\text{H}_2\text{S}_7$	1.721	—	—
$\text{H}_2\text{S}_8$	1.747	—	—

This disproportionation is catalysed by alkali, and even traces dissolved from the surface of glass containers is sufficient to effect deposition of sulfur. They are also degraded by sulfite and by cyanide ions:



The former reaction, in particular, affords a convenient means of quantitative analysis by determination of the  $\text{H}_2\text{S}$  (precipitated as  $\text{CdS}$ ) and iodometric determination of the thiosulfate produced.

### 15.2.3 Halides of sulfur

#### Sulfur fluorides

The seven known sulfur fluorides are quite different from the other halides of sulfur in their stability, reactivity and to some extent even in their stoichiometries; it is therefore convenient to

<sup>116</sup> K. O. CHRISTE, *Inorg. Chem.* **14**, 2230-3 (1975).

<sup>117</sup> R. MINKWITZ, R. KRAUSE, H. HÄRTNER and W. SAWODNY, *Z. anorg. allg. Chem.* **593**, 137-46 (1991).

<sup>118</sup> M. SCHMIDT and W. SIEBERT in *Comprehensive Inorganic Chemistry*, Vol. 2, Chap. 23, pp. 826-42, Pergamon Press, Oxford, 1973.



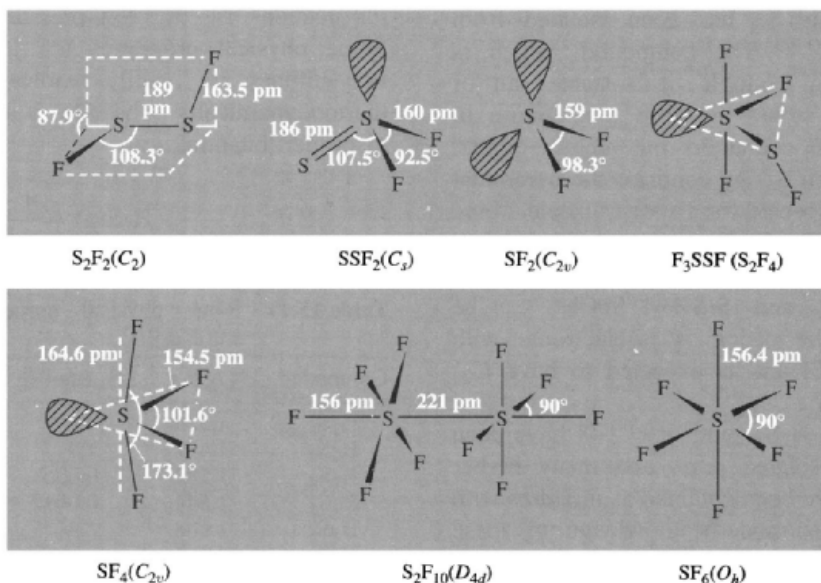


Figure 15.20 Molecular structures of the sulfur fluorides.

consider them separately. Moreover, they have proved a rich field for both structural and theoretical studies since they form an unusually extensive and graded series of covalent molecular compounds in which S has the oxidation states 1, 2, 3, 4, 5 and 6, and in which it also exhibits all coordination numbers from 1 to 6 (if  $\text{SF}_5^-$  is also included). The compounds feature a rare example of structural isomerism amongst simple molecular inorganic compounds ( $\text{FSSF}$  and  $\text{SSF}_2$ ) and also a monomer–dimer pair ( $\text{SF}_2$  and  $\text{F}_3\text{SSF}$ ). The structures and physical properties will be described first, before discussing the preparative routes and chemical reactions.

*Structures and physical properties.* The molecular structure, point group symmetries, and dimensions of the sulfur fluorides are summarized in Fig. 15.20<sup>(119)</sup>  $\text{S}_2\text{F}_2$  resembles  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{S}_2$ ,  $\text{O}_2\text{F}_2$  and  $\text{S}_2\text{X}_2$ , and detailed comparisons of bond distances, bond angles and dihedral angles are instructive. The isomer  $\text{SSF}_2$  (thiothionyl fluoride) features 3-coordinate  $\text{S}^{\text{IV}}$  and 1-coordinate  $\text{S}^{\text{II}}$  and it is notable that the formally

double-bonded S–S distance is very close to that in the singly bonded isomer. The fugitive species  $\text{SF}_2$  has the expected bent configuration in the gas phase but is unique in readily undergoing dimerization by insertion of a second  $\text{SF}_2$  into an S–F bond. The structure of the resulting molecule  $\text{F}_3\text{SSF}$  is, in a sense, intermediate between those of  $\text{S}_2\text{F}_2$  and  $\text{SF}_4$ , being based on a trigonal bipyramid with the equatorial F atom replaced by an SF group. The fact that the  $^{19}\text{F}$  nmr spectrum at  $-100^\circ$  shows four distinct F resonances indicates that the 2 axial F atoms are non-equivalent, implying restricted rotation about the S–S bond.

The structure of  $\text{SF}_4$  is particularly significant. It is based on a trigonal bipyramid with one equatorial position occupied by the lone-pair; this distorts the structure by reducing the equatorial F–S–F bond angle from  $120^\circ$  to  $101.6^\circ$  and by repelling the axial  $\text{F}_{\text{ax}}$  atoms towards  $\text{F}_{\text{eq}}$ . There is also a significant difference between the (long) S– $\text{F}_{\text{ax}}$  and (short) S– $\text{F}_{\text{eq}}$  distances. Again, the low-temperature  $^{19}\text{F}$  nmr spectrum is precisely diagnostic of the  $\text{C}_{2v}$  structure, since the observed doublet of 1:2:1 triplets is consistent only with the two sets of 2 equivalent F atoms in this point group symmetry

<sup>119</sup> F. SEEL, *Adv. Inorg. Chem. Radiochem.* **16**, 297–333 (1974).

Table 15.13 Physical properties of some sulfur fluorides

	FSSF	S=SF <sub>2</sub>	SF <sub>4</sub>	SF <sub>6</sub>	S <sub>2</sub> F <sub>10</sub>
MP/°C	-133	-164.6	-121	-50.54	-52.7
BP/°C	+15	-10.6	-38	-63.8 (subl)	+30
Density(T°C)/g cm <sup>-3</sup>	—	—	1.919(-73°)	1.88(-50°)	2.08(0°)

(<sup>19</sup>F, like <sup>1</sup>H, has nuclear spin  $\frac{1}{2}$ ).<sup>(120)</sup> Thus, an axial lone-pair ( $C_{3v}$ ) would lead to a doublet and a quartet of integrated relative intensity 3:1, whereas all other conceivable symmetries ( $T_d$ ,  $C_{4v}$ ,  $D_{4h}$ ,  $D_{2d}$ ,  $D_{2h}$ ) would give a sharp singlet from the 4 equivalent F atoms. Above -98° the 30 MHz <sup>19</sup>F nmr spectrum of SF<sub>4</sub> gradually broadens and it coalesces at -47° into a single broad resonance which gradually sharpens again to a narrow singlet at higher temperatures; this is due to molecular fluxionality which permits intramolecular interchange of the axial and equatorial F atoms.

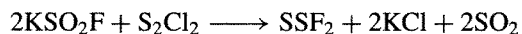
The structure of SF<sub>4</sub> can be rationalized on most of the simple bonding theories; the environment of S has 10 valency electrons and this leads to the observed structure in both valence-bond and electron-pair repulsion models. However, the rather high energy of the 3d orbitals on S make their full participation in bonding via sp<sup>3</sup>d<sub>2</sub> unlikely and, indeed, calculations<sup>(121)</sup> show that there may be as little as 12% d-orbital participation rather than the 50% implied by the scheme sp<sub>x</sub>p<sub>y</sub> + p<sub>z</sub>d<sub>2</sub>. Thus charge-transfer configurations or bonding via sp<sub>x</sub>p<sub>y</sub> + p<sub>z</sub> seem to be better descriptions, the p<sub>z</sub> orbital on S being involved in a 3-centre 4-electron bond with the 2 axial F atoms (cf. XeF<sub>2</sub>, p. 897).

The regular octahedral structure of SF<sub>6</sub> and the related structure of S<sub>2</sub>F<sub>10</sub> (Fig. 15.20) call for little comment except to note the staggered ( $D_{4d}$ ) arrangement of the two sets of F<sub>eq</sub> in S<sub>2</sub>F<sub>10</sub> and the unusually long S-S distance, both features presumably reflecting interatomic repulsion between the F atoms. SF<sub>6</sub> is also of

interest in establishing conclusively that S can be hexavalent. Its great stability (see below) contrasts with the non-existence of SH<sub>4</sub> and SH<sub>6</sub> despite the general similarity in S-F and S-H bond strengths; its existence probably reflects (a) the high electronegativity of F (p. 26), which facilitates the formation of either polar or 3-centre 4-electron bonds as discussed above for SF<sub>4</sub>, and (b) the lower bond energy of F<sub>2</sub> compared to H<sub>2</sub>, which for SH<sub>4</sub> and SH<sub>6</sub> favours dissociation into H<sub>2</sub>S + nH<sub>2</sub>.<sup>(122)</sup> For descriptions of the bonding which involve the use of 3d orbitals on sulfur, a net positive charge on the central atom would contract the d orbitals thereby making them energetically and spatially more favourable for overlap with the fluorine orbitals.

Some physical properties of the more stable sulfur fluorides are in Table 15.13. All are colourless gases or volatile liquids at room temperature. SF<sub>6</sub> sublimates at -63.8° (1 atm) and can only be melted under pressure (-50.8°). It is notable both for its extreme thermal and chemical stability (see below), and also for having a higher gas density than any other substance that boils below room temperature (5.107 times as dense as air).

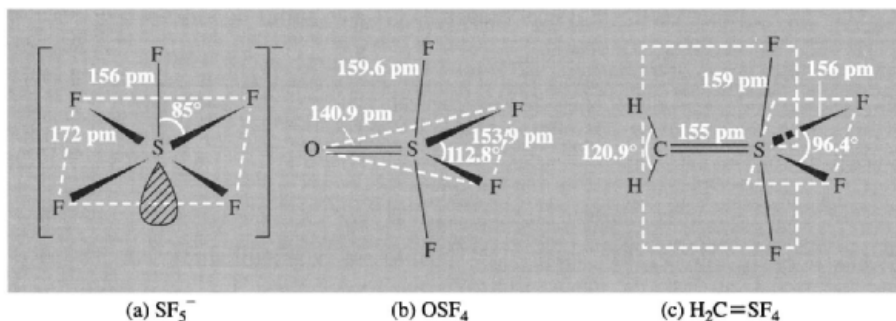
*Synthesis and chemical reactions.* Disulfur difluoride, S<sub>2</sub>F<sub>2</sub>, can be prepared by the mild fluorination of sulfur with AgF in a rigorously dried apparatus at 125°. It is best handled in the gas phase at low pressures and readily isomerizes to thiothionylfluoride, SSF<sub>2</sub>, in the presence of alkali metal fluorides. SSF<sub>2</sub> can be made either by isomerizing S<sub>2</sub>F<sub>2</sub> or directly by the fluorination of S<sub>2</sub>Cl<sub>2</sub> using KF in SO<sub>2</sub>:



<sup>120</sup> F. A. COTTON, J. W. GEORGE and J. S. WAUGH, *J. Chem. Phys.* **28**, 994-5 (1958); E. MUETTERTIES and W. D. PHILLIPS, *J. Am. Chem. Soc.* **81**, 1084-8 (1959).

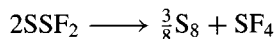
<sup>121</sup> P. J. HAY, *J. Am. Chem. Soc.* **99**, 1003-12 (1977).

<sup>122</sup> G. M. SCHWENZER and H. F. SCHAEFFER, *J. Am. Chem. Soc.* **97**, 1393-7 (1975).

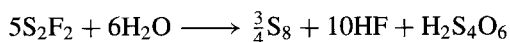


**Figure 15.21** Comparison of the structures of three species in which S has 12 valence electrons: (a) the  $\text{SF}_5^-$  ion in  $\text{RbSF}_5$ , as deduced from X-ray analysis,<sup>(123)</sup> (b)  $\text{OSF}_4$  as deduced from gas-phase electron diffraction<sup>(124)</sup> (note the wider angle  $\text{F}_{\text{eq}}\text{SF}_{\text{eq}}$  when compared with  $\text{SF}_4$  (Fig. 15.20) and the shorter distance  $\text{S}-\text{F}_{\text{ax}}$ ; the angle  $\text{F}_{\text{ax}}\text{SF}_{\text{ax}}$  is  $164.6^\circ$ ), and (c)  $\text{H}_2\text{CSF}_4$  (X-ray crystal structure at  $-160^\circ$ ).<sup>(125)</sup> The angle  $\text{F}_{\text{eq}}\text{SF}_{\text{eq}}$  is significantly smaller than in  $\text{SF}_4$  as is the angle  $\text{F}_{\text{ax}}\text{SF}_{\text{ax}}$  ( $170.4^\circ$ ); the methylene group is coplanar with the axial  $\text{SF}_2$  group as expected for  $p_\pi-d_\pi$   $\text{C}=\text{S}$  overlap and, unlike  $\text{SF}_4$ , the molecule is non-fluxional.

$\text{SSF}_2$  can be heated to  $250^\circ$  but is, in fact, thermodynamically unstable with respect to disproportionation, being immediately transformed to  $\text{SF}_4$  in the presence of acid catalysts such as  $\text{BF}_3$  or  $\text{HF}$ :



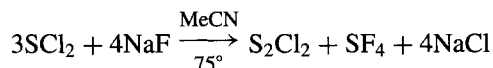
Both  $\text{S}_2\text{F}_2$  and  $\text{SSF}_2$  are rapidly hydrolysed by pure water to give  $\text{S}_8$ ,  $\text{HF}$  and a mixture of polythionic acids  $\text{H}_2\text{S}_n\text{O}_6$  ( $n$  4–6), e.g.:



Alkaline hydrolysis yields predominantly thiosulfate.  $\text{SSF}_2$  burns with a pale-blue flame when ignited, to yield  $\text{SO}_2$ ,  $\text{SOF}_2$  and  $\text{SO}_2\text{F}_2$ .

Sulfur difluoride,  $\text{SF}_2$ , is a surprisingly fugitive species in view of its stoichiometric similarity to the stable compounds  $\text{H}_2\text{S}$  and  $\text{SCl}_2$  (p. 689). It is best made by fluorinating gaseous  $\text{SCl}_2$  with activated  $\text{KF}$  (from  $\text{KSO}_2\text{F}$ ) or with  $\text{HgF}_2$  at  $150^\circ$ , followed by a tedious fractionation from the other sulfur fluorides ( $\text{FSSF}$ ,  $\text{SSF}_2$  and  $\text{SF}_4$ ) which form the predominant products. The chlorofluorides  $\text{ClSSF}$  and  $\text{ClSSF}_3$  are also formed. The compound can only be handled as a dilute gas under rigorously anhydrous conditions or at very low temperatures in a matrix of solid argon, and it rapidly dimerizes to give  $\text{F}_3\text{SSF}$ .

Sulfur tetrafluoride,  $\text{SF}_4$ , though extremely reactive (and valuable) as a selective fluorinating agent, is much more stable than the lower fluorides. It is formed, together with  $\text{SF}_6$ , when a cooled film of sulfur is reacted with  $\text{F}_2$ , but is best prepared by fluorinating  $\text{SCl}_2$  with  $\text{NaF}$  in warm acetonitrile solution:



$\text{SF}_4$  is unusual in apparently acting both as an electron-pair acceptor and an electron-pair donor (amphoteric Lewis acid-base). Thus pyridine forms a stable 1:1 adduct  $\text{C}_5\text{H}_5\text{NSF}_4$  which presumably has a pseudooctahedral (square-pyramidal) geometry. Likewise  $\text{CsF}$  (at  $125^\circ$ ) and  $\text{Me}_4\text{NF}$  (at  $-20^\circ$ ) form  $\text{CsSF}_5$  and  $[\text{NMe}_4]^+[\text{SF}_5]^-$  (Fig. 15.21a). By contrast,  $\text{SF}_4$  behaves as a donor to form 1:1 adducts with many Lewis acids; the stability decreases in the sequence  $\text{SbF}_5 > \text{AsF}_5 > \text{IrF}_5 > \text{BF}_3 > \text{PF}_5 > \text{AsF}_3$ . In view of the discussion on

<sup>123</sup> J. BITTNER, J. FUCHS and K. SEPELT, *Z. anorg. allg. Chem.* **551**, 182–90 (1988).

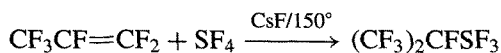
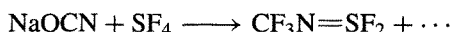
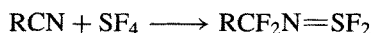
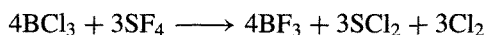
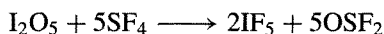
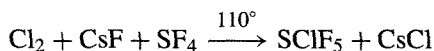
<sup>124</sup> L. HEDBERG and K. HEDBERG, *J. Phys. Chem.* **86**, 598–602 (1982).

<sup>125</sup> H. BOCK, J. E. BOGGS, G. KLEEMANN, D. LENTZ, H. OBERHAMMER, E. M. PETERS, K. SEPELT, A. SIMON and B. SOLOUKI, *Angew. Chem. Int. Edn. Engl.* **18**, 944–5 (1979).

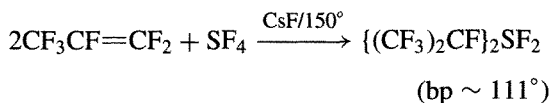
p. 198 it seems likely that SF<sub>4</sub> is acting here not as an S lone-pair donor but as a fluoride ion lone-pair donor and there is, indeed, infrared evidence to suggest that SF<sub>4</sub>.BF<sub>3</sub> is predominantly [SF<sub>3</sub>]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup>.

SF<sub>4</sub> rapidly decomposes in the presence of moisture, being instantly hydrolysed to HF and SO<sub>2</sub>. Despite this it has been increasingly used as a powerful and highly selective fluorinating agent for both inorganic and organic compounds. In particular it is useful for converting ketonic and aldehyde >C=O groups to >CF<sub>2</sub>, and carboxylic acid groups -COOH to -CF<sub>3</sub>. Similarly, ≡P=O groups are smoothly converted to ≡PF<sub>2</sub>, and >P(O)OH groups to >PF<sub>3</sub>. It also undergoes numerous oxidative addition reactions to give derivatives of S<sup>VI</sup>. The simplest of these are direct oxidation of SF<sub>4</sub> with F<sub>2</sub> or ClF (at 380°) to give SF<sub>6</sub> and SCIF<sub>5</sub> respectively. Analogous reactions with N<sub>2</sub>F<sub>4</sub>(*hν*) and F<sub>5</sub>SOOSF<sub>5</sub> yield SF<sub>5</sub>NF<sub>2</sub> and *cis*-SF<sub>4</sub>(OSF<sub>5</sub>)<sub>2</sub> respectively; likewise F<sub>5</sub>SOF (p. 688) yields F<sub>5</sub>SOSF<sub>5</sub>. Direct oxidation of SF<sub>4</sub> with O<sub>2</sub>, however, proceeds only slowly unless catalysed by NO<sub>2</sub>: the product is OSF<sub>4</sub>, which has a trigonal bipyramidal structure like SF<sub>4</sub> itself, but with the equatorial lone-pair replaced by the oxygen atom (Fig. 15.21b). A similar structure is adopted by the more recently prepared methylene compound H<sub>2</sub>C=SF<sub>4</sub> (Fig. 15.21c);<sup>(125)</sup> this is made by treating SF<sub>5</sub>-CH<sub>2</sub>Br with LiBu<sup>n</sup> at -110° and is more stable than the isoelectronic P or S ylides or metal carbene complexes, being stable in the gas phase up to 650° at low pressures.

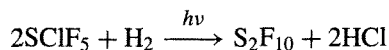
Some other reactions of SF<sub>4</sub> are:



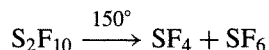
(bp 46°)



Disulfur decafluoride, S<sub>2</sub>F<sub>10</sub>, is obtained as a byproduct of the direct fluorination of sulfur to SF<sub>6</sub> but is somewhat tedious to separate and is more conveniently made by the photolytic reduction of SCIF<sub>5</sub> (prepared as above):



It is intermediate in reactivity between SF<sub>4</sub> and the very inert SF<sub>6</sub>. Unlike SF<sub>4</sub> it is not hydrolysed by water or even by dilute acids or alkalis and, unlike SF<sub>6</sub>, it is extremely toxic. It disproportionates readily at 150° probably by a free radical mechanism involving SF<sub>5</sub><sup>•</sup> (note the long, weak S-S bond; Fig. 15.20):



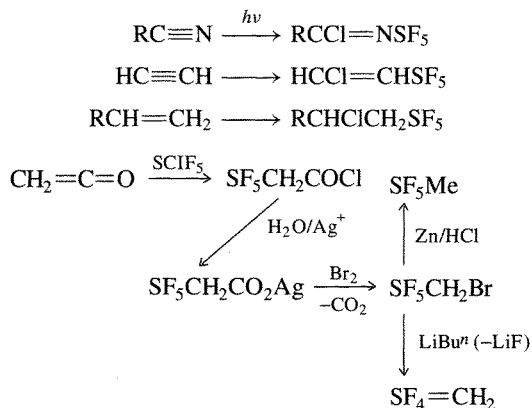
Similarly it reacts readily with Cl<sub>2</sub> and Br<sub>2</sub> to give SCIF<sub>5</sub> and SBrF<sub>5</sub>. It oxidizes KI (and I<sub>3</sub><sup>-</sup>) in acetone solution to give iodine (note SF<sub>4</sub> converts acetone to Me<sub>2</sub>CF<sub>2</sub>). S<sub>2</sub>F<sub>10</sub> reacts with SO<sub>2</sub> to give F<sub>5</sub>SSO<sub>2</sub>F and with NH<sub>3</sub> to give N≡SF<sub>3</sub>.

Sulfur hexafluoride is unique in its stability and chemical inertness: it is a colourless, odourless, tasteless, unreactive, non-flammable, non-toxic, insoluble gas prepared by burning sulfur in an atmosphere of fluorine. Because of its extraordinary stability and excellent dielectric properties it is extensively used as an insulating gas for high-voltage generators and switch gear: at a pressure of 2–3 bars it withstands 1.0–1.4 MV across electrodes 50 mm apart without breakdown, and at 10 bars it is used for high-power underground electrical transmission systems at 400 V and above. However, there is now some environmental concern at its use as an electrical transformer fluid and as an inert blanketing gas in magnesium metal casting, since even minute amounts may contribute to an atmospheric greenhouse effect (it is 6800 times as potent as CO<sub>2</sub>).

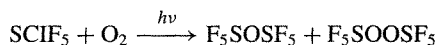
SF<sub>6</sub> can be heated to 500° without decomposition, and is unattacked by most metals, P, As, etc., even when heated. It is also unreactive towards

high-pressure steam presumably as a result of kinetic factors since the gas-phase reaction  $\text{SF}_6 + 3\text{H}_2\text{O} \longrightarrow \text{SO}_3 + 6\text{HF}$  should release some  $460 \text{ kJ mol}^{-1}$  ( $\Delta G^\circ \sim 200 \text{ kJ mol}^{-1}$ ). By contrast, reaction with  $\text{H}_2\text{S}$  yields sulfur and HF. Hot HCl and molten KOH at  $500^\circ$  are without effect. Boiling Na attacks  $\text{SF}_6$  to yield  $\text{Na}_2\text{S}$  and NaF; indeed, this reaction can be induced to go rapidly even at room temperature or below in the presence of biphenyl dissolved in glyme (1,2-dimethoxyethane). It is also reduced by Na/liq  $\text{NH}_3$  and, more slowly, by  $\text{LiAlH}_4/\text{Et}_2\text{O}$ .  $\text{Al}_2\text{Cl}_6$  at  $200^\circ$  yields  $\text{AlF}_3$ ,  $\text{Cl}_2$ , and sulfur chlorides. Recent experiments<sup>(126)</sup> indicate that  $\text{SF}_6$  becomes much more reactive at higher temperatures and pressures; for example  $\text{PF}_3$  is quantitatively oxidized to  $\text{PF}_5$  at  $500^\circ$  and 300 bars, and to a mixture of  $\text{PF}_5$  and  $\text{SPF}_3$  at  $\sim 380^\circ$  and 1800–3600 bars.

Derivatives of  $\text{SF}_6$  are rather more reactive:  $\text{S}_2\text{F}_{10}$  and  $\text{SClF}_5$  have already been mentioned. Further synthetically useful reactions of this latter compound are:



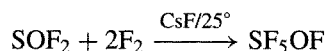
p. 687



$\text{SClF}_5$  is readily attacked by other nucleophiles, e.g.  $\text{OH}^-$  but is inert to acids.  $\text{SF}_5\text{OH}$  and  $\text{SF}_5\text{OOH}$  are known.

The very reactive yellow  $\text{SF}_5\text{OF}$ , which is one of the few known hypofluorites, can be made by

the catalytic reaction:



In the absence of CsF the product is  $\text{SOF}_4$  (p. 687) and this can then be isomerized in the presence of CsF to give a second hypofluorite,  $\text{SF}_3\text{OF}$ . Derivatives of  $-\text{SF}_5$  are usually reactive volatile liquids or gases, e.g.:

Compound	$\text{F}_5\text{SCl}$	$\text{F}_5\text{SBr}$	$(\text{F}_5\text{S})_2\text{O}$	$(\text{F}_5\text{SO})_2$
MP/ $^\circ\text{C}$	-64	-79	-118	-95.4
BP/ $^\circ\text{C}$	-21	+3.1	+31	+49.4

Compound	$\text{F}_5\text{SNF}_2^{(a)}$	$(\text{F}_5\text{S})_2$	$\text{F}_5\text{SOF}$
MP/ $^\circ\text{C}$	-	-52.7	-86
BP/ $^\circ\text{C}$	-18	+30.0	-35.1

<sup>(a)</sup>See ref. 127 for  $\text{F}_5\text{SNClF}$ ,  $\text{F}_5\text{SNHF}$  and  $\text{F}_4\text{S}=\text{NF}$ , and ref. 128 for  $\text{F}_5\text{SN}=\text{SClF}$

Of these,  $(\text{F}_5\text{SO}-)_2$  is an amusing example of a compound accidentally prepared as a byproduct of  $\text{SF}_6$  and  $\text{S}_2\text{F}_{10}$  due to the fortuitous presence of traces of molecular oxygen in the gaseous fluorine used to fluorinate sulfur. A small amount of material boiling somewhat above  $\text{S}_2\text{F}_{10}$  and having a molecular weight some 32 units higher was isolated. [How would you show that it was not  $\text{S}_3\text{F}_{10}$ , and that its structure was  $\text{F}_5\text{SOOSF}_5$  rather than one of the 8 possible isomers of  $\text{F}_4\text{S}(\text{OF})-\text{SF}_4(\text{OF})$  or  $\text{F}_4\text{S}(\text{OF})-\text{OSF}_5$ ?]<sup>(129)</sup>

Numerous other highly reactive oxofluoro-sulfur compounds have been prepared but their chemistry, though sometimes hazardous because of a tendency to explosion, introduces no new principles. Some examples are:

Thionyl fluorides:  $\text{OSF}_2$ ,  $\text{OSFCl}$ ,  $\text{OSFBr}$ ,  $\text{OSF}(\text{OM})$ .

Sulfuryl fluorides:  $\text{O}_2\text{SF}_2$ ,  $\text{FSO}_2-\text{O}-\text{SO}_2\text{F}$ ,  $\text{FSO}_2-\text{O}-\text{SO}_2-\text{O}-\text{SO}_2\text{F}$ ,  $\text{FSO}_2-\text{OO}-\text{SO}_2\text{F}$ ,  $\text{FSO}_2-\text{OO}-\text{SF}_5$ .

<sup>127</sup> D. D. DESMARTEAU, H. H. EYSEL, H. OBERHAMMER and H. GÜNTHER, *Inorg. Chem.* **21**, 1607–16 (1982).

<sup>128</sup> J. S. THRASHER, N. S. HOSMANE, D. E. MAURER and A. F. CLIFFORD, *Inorg. Chem.* **21**, 2506–8 (1982).

<sup>129</sup> R. B. HARVEY and S. H. BAUER, *J. Am. Chem. Soc.* **76**, 859–64 (1954).

<sup>126</sup> A. P. HAGEN and D. L. TERRELL, *Inorg. Chem.* **20**, 1325–6 (1981).

Other peroxy compounds:<sup>(130)</sup> SF<sub>5</sub>OOC(O)F,  
 SF<sub>5</sub>OSF<sub>4</sub>OOSF<sub>5</sub>, SF<sub>5</sub>OSF<sub>4</sub>OOSF<sub>4</sub>OSF<sub>5</sub>,  
 CF<sub>3</sub>OSF<sub>4</sub>OOSF<sub>5</sub>, CF<sub>3</sub>OSF<sub>4</sub>OOSF<sub>4</sub>OCF<sub>3</sub>,  
 (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>O<sub>2</sub>, HOSO<sub>2</sub>OOCF<sub>3</sub>,  
 CF<sub>3</sub>OOSO<sub>2</sub>OCF<sub>3</sub>.

Fluorosulfuric acid:<sup>(131)</sup> FSO<sub>2</sub>(OH), FSO<sub>3</sub><sup>-</sup>.

Of these the most extensively studied is fluorosulfuric acid, made by direct reaction of SO<sub>3</sub> and HF. Its importance derives from its use as a solvent system and from the fact that its mixtures with SbF<sub>5</sub> and SO<sub>3</sub> are amongst the strongest known acids (superacids, p. 570). Anhydrous HSO<sub>3</sub>F is a colourless, dense, mobile liquid which fumes in moist air: mp -89.0°, bp 162.7°; *d*<sub>25</sub> 1.726 g cm<sup>-3</sup>, *η*<sub>25</sub> 1.56 centipoise, *κ*<sub>25</sub> 1.085 × 10<sup>-4</sup> ohm<sup>-1</sup> cm<sup>-1</sup>.

Attention should also be directed to the growing number of perfluorocarbon-sulfur species which feature single, double or even triple C-S bonds, e.g.:

Single: (F<sub>5</sub>S)<sub>2</sub>CF<sub>2</sub>,<sup>(132)</sup> F<sub>4</sub>SCF<sub>2</sub>SF<sub>4</sub>CF<sub>2</sub>,<sup>(132)</sup>  
 [(F<sub>5</sub>S)C(CF<sub>3</sub>)<sub>2</sub>]<sup>-</sup>,<sup>(133)</sup> [(F<sub>5</sub>S)<sub>2</sub>C(CF<sub>3</sub>)]<sup>-</sup>,<sup>(133)</sup>  
 [F<sub>3</sub>SCF<sub>2</sub>S(F<sub>3</sub>)F]<sup>-</sup>;<sup>(134)</sup> see also footnote on  
 p. 690;

Double:

(F<sub>5</sub>S)(F<sub>3</sub>C)C=SF<sub>2</sub>,<sup>(135)</sup> (F<sub>3</sub>C)<sub>2</sub>C=SF<sub>2</sub>,<sup>(135)</sup>

Triple: (F<sub>3</sub>C)C≡SF<sub>3</sub>,<sup>(136-138)</sup> (F<sub>5</sub>S)C≡SF<sub>3</sub>.<sup>(139)</sup>

<sup>130</sup> R. A. DE MARCO and J. M. SHREEVE, *Adv. Inorg. Chem. Radiochem.* **16**, 109-76 (1974).

<sup>131</sup> A. W. JACHE, *Adv. Inorg. Chem. Radiochem.* **16**, 177-200 (1974).

<sup>132</sup> K. D. GUPTA, R. MEWS, A. WATERFELD, J. M. SHREEVE and H. OBERHAMMER, *Inorg. Chem.* **25**, 275-8 (1986).

<sup>133</sup> J. BITTNER, R. GERHARDT, K. MOOCK and K. SEPELT, *Z. anorg. allg. Chem.* **602**, 89-96 (1991).

<sup>134</sup> D. VIETS, W. HEILEMANN, A. WATERFELD, R. MEWS, S. BESSER, R. HERBST-IRMER, G. M. SHELDRIK and W.-D. STOHRER, *J. Chem. Soc., Chem. Commun.*, 1017-9 (1992).

<sup>135</sup> R. DAMERIUS, K. SEPELT and J. S. THRASHER, *Angew. Chem. Int. Edn. Engl.* **28**, 769-70 (1989).

<sup>136</sup> W. SAAK, G. HENKEL and S. POHL, *Angew. Chem. Int. Edn. Engl.* **23**, 150 (1984).

<sup>137</sup> B. PÖTTER, K. SEPELT, A. SIMON, E.-M. PETERS and B. HETTICH, *J. Am. Chem. Soc.* **107**, 980-5 (1985).

<sup>138</sup> D. A. DIXON and B. E. SMART, *J. Am. Chem. Soc.* **108**, 2688-91 (1986).

<sup>139</sup> R. GERHARDT, T. GRELBIG, J. BUSCHMANN, P. LUGER and K. SEPELT, *Angew. Chem. Int. Edn. Engl.* **27**, 1534-6 (1988).

Also notable are sulfur cyanide fluorides such as SF<sub>3</sub>CN,<sup>(140)</sup> SF<sub>2</sub>(CN)<sub>2</sub><sup>(140)</sup> and SF<sub>5</sub>CN<sup>(141,142)</sup> and the sulfinyl cyanide fluoride FS(O)CN.<sup>(140)</sup>

### Chlorides, bromides and iodides of sulfur

Sulfur is readily chlorinated by direct reaction with Cl<sub>2</sub> but the simplicity of the products obtained belies the complexity of the mechanisms involved. The reaction was first investigated by C. W. Scheele in 1774 and has been extensively studied since because of its economic importance (see below) and its intrinsic physicochemical interest. Direct chlorination of molten S followed by fractional distillation yields disulfur dichloride (S<sub>2</sub>Cl<sub>2</sub>) a toxic, golden-yellow liquid of revolting smell: mp -76°, bp 138°, *d*(20°) 1.677 g cm<sup>-3</sup>. The molecule has the expected C<sub>2</sub> structure (like S<sub>2</sub>F<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, etc.) with S-S 195 pm, S-Cl 206 pm, angle Cl-S-S 107.7°, and a dihedral angle of 85.2°.<sup>(143)</sup> Further chlorination of S<sub>2</sub>Cl<sub>2</sub>, preferably in the presence of a trace of catalyst such as FeCl<sub>3</sub>, yields the more-volatile, cherry-red liquid sulfur dichloride, SCl<sub>2</sub>: mp -122°, bp 59°, *d*(20°) 1.621 g cm<sup>-3</sup>. SCl<sub>2</sub> resembles S<sub>2</sub>Cl<sub>2</sub> in being foul-smelling and toxic, but is rather unstable when pure due to the decomposition equilibrium 2SCl<sub>2</sub> ⇌ S<sub>2</sub>Cl<sub>2</sub> + Cl<sub>2</sub>. However, it can be stabilized by the presence of as little as 0.01% PCl<sub>5</sub> and can be purified by distillation at atmospheric pressure in the presence of 0.1% PCl<sub>5</sub>.<sup>(144)</sup> The sulfur dichloride molecule is nonlinear (C<sub>2v</sub>) as expected, with S-Cl 201 pm and angle Cl-S-Cl 103°.

S<sub>2</sub>Cl<sub>2</sub> and SCl<sub>2</sub> both react readily with H<sub>2</sub>O to give a variety of products such as

<sup>140</sup> J. JACOBS and H. WILLNER, *Z. anorg. allg. Chem.* **619**, 1221-6 (1993).

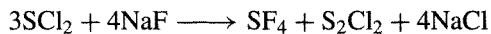
<sup>141</sup> O. LÖSKING and H. WILLNER, *Angew. Chem. Int. Edn. Engl.* **28**, 1255-6 (1989).

<sup>142</sup> J. S. THRASHER and K. V. MADAPPAT *Angew. Chem. Int. Edn. Engl.* **28**, 1256-8 (1989).

<sup>143</sup> C. J. MARSDEN, R. D. BROWN, and P. D. GODFREY, *J. Chem. Soc., Chem. Commun.*, 399-401 (1979).

<sup>144</sup> R. J. ROSSEN and F. R. WHITT, *J. Appl. Chem.* **10**, 229-37 (1960); see also the following paper (pp. 237-46) for large-scale distillation unit.

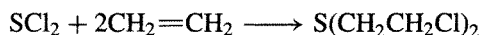
$\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{SO}_4$  and the polythionic acids  $\text{H}_2\text{S}_x\text{O}_6$ . Oxidation of  $\text{SCl}_2$  yields thionyl chloride ( $\text{OSCl}_2$ ) and sulfuryl chloride ( $\text{O}_2\text{SCl}_2$ ) (see Section 15.2.4). Reaction with  $\text{F}_2$  produces  $\text{SF}_4$  and  $\text{SF}_6$  (p. 686), whereas fluorination with  $\text{NaF}$  is accompanied by some disproportionation:



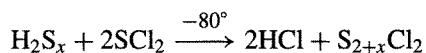
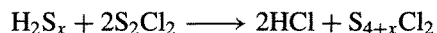
As indicated on p. 686, fluorination of  $\text{S}_2\text{Cl}_2$  with  $\text{KF}/\text{SO}_2$  occurs with concurrent isomerization to  $\text{SSF}_2$ . Both  $\text{S}_2\text{Cl}_2$  and  $\text{SCl}_2$  react with atomic N (p. 413) to give  $\text{NSCl}$  as the first step, and this can then react further with  $\text{S}_2\text{Cl}_2$  to give the ionic heterocyclic compound  $\text{S}_3\text{N}_2\text{Cl}^+\text{Cl}^-$  (p. 739). By contrast, reaction of  $\text{S}_2\text{Cl}_2$  with  $\text{NH}_4\text{Cl}$  at  $160^\circ$  (or with  $\text{NH}_3 + \text{Cl}_2$  in boiling  $\text{CCl}_4$ ) yields the cluster compound  $\text{S}_4\text{N}_4$  (p. 722). Treatment of  $\text{S}_2\text{Cl}_2$  with  $\text{Hg}(\text{SCN})_2$  yields colourless crystals of  $\text{S}_4(\text{CN})_4$ , mp  $-2^\circ$ , which are composed of unbranched chain molecules  $\text{NCSSSSCN}$  with essentially linear NCS groups ( $177.5^\circ$ ,  $178.4^\circ$ ) and the angles CSS  $98.6^\circ$  and SSS  $106.5^\circ$ ; interatomic distances are within the expected ranges, viz.  $\text{N}\equiv\text{C}$  113.4, C–S 169.6, outer S–S 206.8 and inner S–S 201.7 pm.<sup>(145)</sup>  $\text{SCl}_2$  acts as a ligand to Pd and Pt in the yellow 4-coordinate complex *trans*- $[\text{PdCl}_2(\text{SCl}_2)_2]$  and the red 6-coordinate complex *trans*- $[\text{PtCl}_4(\text{SCl}_2)_2]$ .<sup>(146)</sup> These are formed when either Pd or Pt metal is heated in a quartz ampoule with elemental S and  $\text{Cl}_2$  at  $200^\circ\text{C}$  for 4 days, and they decompose into  $\text{SCl}_2$  and  $\text{PdCl}_2$  or  $\text{PtCl}_4$ , respectively, on being heated.

$\text{S}_2\text{Cl}_2$  and  $\text{SCl}_2$  are important industrial chemicals. The main use for  $\text{S}_2\text{Cl}_2$  is in the vapour-phase vulcanization of certain rubbers, but other uses include its chlorinating action in the preparation of mono- and di-chlorohydrins, and the opening of some minerals in extractive metallurgy. Some idea of the scale of production can be gauged from the fact that  $\text{S}_2\text{Cl}_2$  is shipped in 50-tonne tank cars; smaller quantities are transported in drums containing 300 or 60 kg

of the liquid. Its less-stable homologue  $\text{SCl}_2$  is notable for its ready addition across olefinic double bonds: e.g., thiochlorination of ethene yields the notorious vesicant, mustard gas:



The compounds  $\text{SCl}_2$  and  $\text{S}_2\text{Cl}_2$  can be thought of as the first two members of an extended series of dichlorosulfanes  $\text{S}_n\text{Cl}_2$ . The lower electronegativity of Cl (compared with F) and the lower S–Cl bond energy (compared with S–F) enable the natural catenating propensity of S to have full reign and a series of dichlorosulfanes can be prepared in which S–S bonds in sulfur chains (and rings) can be broken and the resulting  $-\text{S}_n-$  oligomers stabilized by the formation of chain-terminating S–Cl bonds. The first eight members with  $n = 1 - 8$  have been isolated as pure compounds, and mixtures up to perhaps  $\text{S}_{100}\text{Cl}_2$  are known.<sup>†</sup> Specific compounds have been made by F. Fehér's group using the polysulfanes as starting materials (p. 683).<sup>(147)</sup>



The dichlorosulfanes are yellow to orange-yellow viscous liquids with an irritating odour. They are thermally and hydrolytically unstable.  $\text{S}_3\text{Cl}_2$  boils at  $31^\circ$  ( $10^{-4}$  mmHg) and has a density of  $1.744 \text{ g cm}^{-3}$  at  $20^\circ$ . Higher homologues have

<sup>†</sup> Several related series of compounds are also known in which Cl is replaced by a pseudohalogen such as  $-\text{CF}_3$  or  $-\text{C}_2\text{F}_5$ , e.g.  $\text{S}_n(\text{CF}_3)_2$  ( $n = 1-4$ ),  $\text{CF}_3\text{S}_n\text{C}_2\text{F}_5$  ( $n = 2-4$ ), and  $\text{S}_n(\text{C}_2\text{F}_5)_2$  ( $n = 2-4$ ). These can be prepared by the reaction of  $\text{CF}_3\text{I}$  and S vapour in a glow discharge followed by fractionation and glc separation; other routes include reaction of  $\text{CS}_2$  with  $\text{IF}_5$  at  $60-200^\circ$ , reaction of  $\text{CF}_3\text{I}$  with sulfur at  $310^\circ$ , and fluorination of  $\text{SCl}_2$  or related compounds with  $\text{NaF}$  or  $\text{KF}$  at  $150-250^\circ$ . (See, for example, T. Yasumura and R. J. Lagow, *Inorg. Chem.* **17**, 3108–10 (1978).)

<sup>147</sup> F. FEHÉR, pp. 370–9 in G. BRAUER (ed.), *Handbook of Preparative Inorganic Chemistry*, 2nd edn., Vol. 1, Academic Press, New York, 1963.

<sup>145</sup> R. STEUDEL, K. BERGEMANN and M. KUSTOS, *Z. anorg. allg. Chem.* **620**, 117–20 (1994).

<sup>146</sup> M. PAULUS and G. THIELE, *Z. anorg. allg. Chem.* **588**, 69–76 (1990).

even higher densities:

$n$ in $S_nCl_2$	1	2	3	4
Density(20°)/g cm <sup>-3</sup>	1.621	1.677	1.744	1.777
$n$ in $S_nCl_2$	5	6	7	8
Density(20°)/g cm <sup>-3</sup>	1.802	1.822	1.84	1.85

The higher chlorides of S (unlike the higher fluorides) are very unstable and poorly characterized. There is no evidence for molecular chloro analogues of SF<sub>4</sub>, S<sub>2</sub>F<sub>10</sub> and SF<sub>6</sub>, though SClF<sub>5</sub> is known (p. 687). Chlorination of SCl<sub>2</sub> by liquid Cl<sub>2</sub> at -78° yields a powdery off-white solid which begins to decompose when warmed above -30°. It analyses as SCl<sub>4</sub> and is generally formulated as SCl<sub>3</sub><sup>+</sup>Cl<sup>-</sup>, but little reliable structural work has been done on it. Consistent with this ionic formulation, reaction of SCl<sub>4</sub> with Lewis acids results in the formation of stable adducts; e.g. AlCl<sub>3</sub> yields the white solid SCl<sub>4</sub>.AlCl<sub>3</sub> which has been shown by vibrational spectroscopy on both the solid and the melt (125°) to be [SCl<sub>3</sub>]<sup>+</sup>[AlCl<sub>4</sub>]<sup>-</sup>.<sup>(148)</sup> The compound [SCl<sub>3</sub>]<sup>+</sup>[ICl<sub>4</sub>]<sup>-</sup> is also known (p. 693).<sup>(149)</sup> As expected from a species that is isoelectronic with PCl<sub>3</sub> the cation is pyramidal; dimensions are: S-Cl (average) 198.5 pm, angle Cl-S-Cl 101.3° (cf. PCl<sub>3</sub>: P-Cl 204.3 pm, angle Cl-P-Cl 100.1°). Other compounds containing [SCl<sub>3</sub>]<sup>+</sup> which have been characterized spectroscopically and by X-ray crystallography include those with [SbCl<sub>6</sub>]<sup>-</sup>, [UCl<sub>6</sub>]<sup>-</sup> and [AsF<sub>6</sub>]<sup>-</sup>.<sup>(150)</sup>

Sulfur bromides are but poorly characterized and there are few reliable data on them. SBr<sub>2</sub> probably does not exist at room temperature but has been claimed as a matrix-isolated product when a mixture of S<sub>2</sub>Cl<sub>2</sub>/SCl<sub>2</sub>:Br<sub>2</sub>:Ar in the ratio 1:1:150 is passed through an 80-W microwave discharge and the product condensed on a CsI

window at 9 K.<sup>(151)</sup> The dibromosulfanes S<sub>n</sub>Br<sub>2</sub> ( $n = 2-8$ ) are formed by the action of anhydrous HBr on the corresponding chlorides.<sup>(147)</sup> The best characterized compound (which can also be made directly from the elements at 100°C) is the garnet-red oily liquid S<sub>2</sub>Br<sub>2</sub> isostructural with S<sub>2</sub>Cl<sub>2</sub> (S-S 198 pm, S-Br 224 pm, angle Br-S-S 105°, dihedral angle 84 ± 11°). It has mp -46°, bp(0.18 mmHg) 54°, and  $d(20^\circ)$  2.629 g cm<sup>-3</sup>, but even at room temperature S<sub>2</sub>Br<sub>2</sub> tends to dissociate into its elements. Interestingly, the higher homologues have progressively lower densities (cf. S<sub>n</sub>Cl<sub>2</sub>). The unusual ionic compound [BrSSSBBr<sub>2</sub>]<sup>+</sup>[AsF<sub>6</sub>]<sup>-</sup> can be formed by reacting stoichiometric amounts of S, Br<sub>2</sub> and AsF<sub>5</sub> in liquid SO<sub>2</sub>.

$n$ in S <sub>n</sub> Br <sub>2</sub>	2	3	4	5	6	7	8
Density(20°)/g cm <sup>-3</sup>	2.629	2.52	2.47	2.41	2.36	2.33	2.30

Sulfur iodides are a topic of considerable current interest, although compounds containing S-I bonds were, in fact, unknown until fairly recently. The failure to prepare sulfur iodides by direct reaction of the elements probably reflects the comparative weakness of the S-I bond: an experimental value is not available but extrapolation from representative values for the bond energies of other S-X bonds leads to a value of ~170 kJ mol<sup>-1</sup>:

Bond Energy/ kJ mol <sup>-1</sup>	S-F	S-Cl	S-Br	S-I	S-S	I-I
	327	271	218	(~170)	225	150

The data indicate that formation of SI<sub>2</sub> from  $\frac{1}{8}S_8 + I_2$  and the formation of S<sub>2</sub>I<sub>2</sub> from  $\frac{1}{4}S_8 + I_2$  are both endothermic to the extent of ~35 kJ mol<sup>-1</sup>, implying that successful synthesis of these compounds must employ kinetically controlled routes to obviate decomposition back to the free elements.

Pure S<sub>2</sub>I<sub>2</sub> was first isolated (as a dark reddish-brown solid) following the reaction of S<sub>2</sub>Cl<sub>2</sub> with

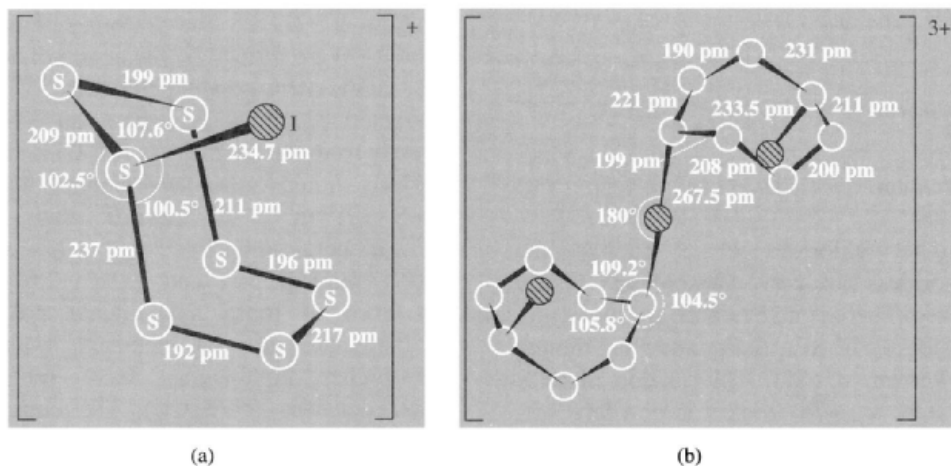
<sup>148</sup> G. MAMANTOV, R. MARASSI, F. W. POULSON, S. E. SPRINGER, J. P. WIAUX, R. HUGLEN and N. R. SMYLN, *J. Inorg. Nuclear Chem.* **41**, 260-1 (1979).

<sup>149</sup> A. J. EDWARDS, *J. Chem. Soc., Dalton Trans.*, 1723-5 (1978).

<sup>150</sup> B. H. CHRISTIAN, M. J. COLLINS, R. J. GILLESPIE and J. F. SAWYER, *Inorg. Chem.* **25**, 777-88 (1986), and references cited therein.

<sup>151</sup> M. FEUERHAN and G. VAHL, *Inorg. Nuclear Chem. Lett.* **16**, 5-8 (1980).



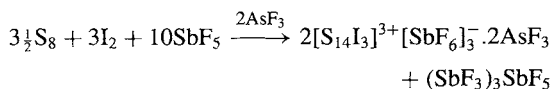


**Figure 15.22** (a) Structure of the iodocycloheptasulfur cation in  $[\text{S}_7\text{I}]^+[\text{SbF}_6]^-$ . The S–S–S angles in the  $\text{S}_7$  ring are in the range  $102.5\text{--}108.4^\circ$  (mean  $105.6^\circ$ ).<sup>(154)</sup> (b) Structure of the centrosymmetric cation  $[(\text{S}_7\text{I})_2\text{I}]^{3+}$  showing similar dimensions to those in  $[\text{S}_7\text{I}]^+$ .<sup>(156)</sup>

$\text{HI}/\text{N}_2$  in a freon solvent of  $-78^\circ$  in the presence of catalytic amounts of added  $\text{I}_2$ .<sup>(152)</sup> The darker brown solid  $\text{OSI}_2$  was formed similarly from  $\text{OSCl}_2$ .  $\text{S}_2\text{I}_2$  and  $\text{OSI}_2$  are both thermally unstable and decompose rapidly above about  $-30^\circ$  into S,  $\text{I}_2$  (and also  $\text{SO}_2$  in the case of  $\text{OSI}_2$ ).<sup>(152)</sup>  $\text{S}_2\text{I}_2$  was assigned  $\text{C}_2$  symmetry (like  $\text{S}_2\text{F}_2$ , p. 684) on the basis of its vibrational spectrum.<sup>(153)</sup>

The first X-ray crystal structure of a species containing an S–I bond was of the curious and unexpected cation  $[\text{S}_7\text{I}]^+$  which was found in the dark-orange compound  $[\text{S}_7\text{I}]^+[\text{SbF}_6]^-$  formed when iodine and sulfur react in  $\text{SbF}_5$  solution.<sup>(154)</sup> The structure of the cation is shown in Fig. 15.22a and features an  $\text{S}_7$  ring with alternating S–S distances and a pendant iodine atom; the conformation of the ring is the same as in  $\text{S}_7$ ,  $\text{S}_8$ , and  $\text{S}_8\text{O}$  (p. 696). The same cation was

found in  $[\text{S}_7\text{I}]_4^+[\text{S}_4]^{2+}[\text{AsF}_6]_6^-$ <sup>(155)</sup> and a similar motif forms part of the iodo-bridged species  $[(\text{S}_7\text{I})_2\text{I}]^{3+}$  (Fig. 15.22b);<sup>(156)</sup> this latter cation was formed during the reaction of  $\text{S}_8$  and  $\text{I}_2$  with  $\text{SbF}_5$  in the presence of  $\text{AsF}_3$  according to the reaction stoichiometry:



The very long S– $\text{I}_\mu$  bonds in the linear S–I–S bridge (267.5 pm) are notable and have been interpreted in terms of an S–I bond order of  $\frac{1}{2}$ . Even weaker  $\text{S} \cdots \text{I}$  interactions occur in the cation  $[\text{S}_2\text{I}_4]^{2+}$  which could, indeed, alternatively be regarded as an  $\text{S}_2^{2+}$  cation coordinated side-on by two  $\text{I}_2$  molecules (Fig. 15.23).<sup>(157)</sup> This

<sup>152</sup> D. K. PADMA, *Indian Journal of Chemistry* **12**, 417–8 (1974).

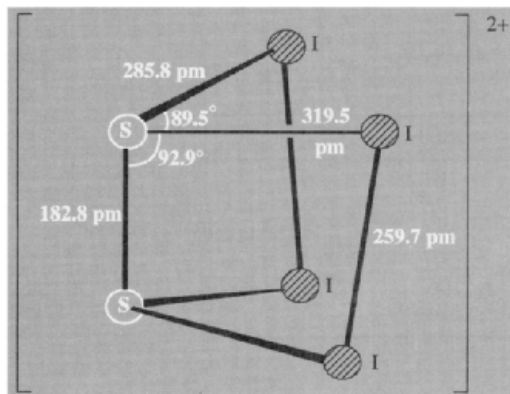
<sup>153</sup> V. G. VAHL and R. MINKWITZ, *Inorg. Nuclear Chem. Lett.* **13**, 213–5 (1977).

<sup>154</sup> J. PASSMORE, P. TAYLOR, T. K. WHIDDEN and P. S. WHITE, *J. Chem. Soc., Chem. Commun.*, 689 (1976). J. PASSMORE, G. SUTHERLAND, P. TAYLOR, T. K. WHIDDEN and P. S. WHITE, *Inorg. Chem.* **20**, 3839–45 (1981). The cation is also one of the products formed when an excess of S reacts with  $[\text{I}_3]^+[\text{AsF}_6]^-$  or  $[\text{I}_3]^+[\text{As}_2\text{F}_{11}]^-$  or  $\text{AsF}_5/\text{I}_2$ , or when  $[\text{S}_{16}]^{2+}[\text{SbF}_6]_2^-$  is iodinated with an excess of iodine.

<sup>155</sup> J. PASSMORE, G. SUTHERLAND and P. S. WHITE, *J. Chem. Soc., Chem. Commun.*, 330–1 (1980). (See also *Inorg. Chem.* **21**, 2717–23 (1982).)

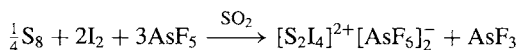
<sup>156</sup> J. PASSMORE, G. SUTHERLAND and P. S. WHITE, *J. Chem. Soc., Chem. Commun.*, 901–2 (1979). (See also *Inorg. Chem.* **21**, 2717–23 (1982).)

<sup>157</sup> J. PASSMORE, G. SUTHERLAND, T. WHIDDEN and P. S. WHITE, *J. Chem. Soc., Chem. Commun.*, 289–90 (1980). M. P. MURCHIE, J. P. JOHNSON, J. PASSMORE, G. W. SUTHERLAND, M. TAJIK, T. K. WHIDDEN, P. S. WHITE and F. GREIN, *Inorg. Chem.* **31**, 273–83 (1992). See also T. KLAPÖTKE and J. PASSMORE, *Accounts Chem. Research* **22**, 234–240 (1989).



**Figure 15.23** Structure of the  $[\text{S}_2\text{I}_4]^{2+}$  cation of  $C_2$  symmetry, showing the very short S–S distance and the rather short I–I distances; note also the S–I distances which are even longer than in the weak charge transfer complex  $[(\text{H}_2\text{N}_2\text{CS})_2\text{I}]^+$  (262.9 pm). The nonbonding  $\text{I}\cdots\text{I}$  distance is 426.7 pm.

curious right triangular prismatic conformation (notably at variance with that in the isoelectronic  $\text{P}_2\text{I}_4$  molecule) is associated with a very short S–S bond (bond order  $2\frac{1}{3}$ ) and rather short I–I distances (bond order  $1\frac{1}{3}$ ). The cation is formed in  $\text{AsF}_5/\text{SO}_2$  solution according to the equation:



Other species containing S–I bonds that have been characterized include the pseudopolyhalide anions  $[\text{I}(\text{SCN})_2]^-$  and  $[\text{I}_2(\text{SCN})]^-$ ,<sup>(158)</sup> and the dimethyliodosulfonium(IV) salts of  $[\text{Me}_2\text{SI}]^+$  with  $[\text{AsF}_6]^-$  and  $[\text{SbCl}_6]^-$  (which latter are thermally unstable above about  $-20^\circ$ ).<sup>(159)</sup>

We conclude this section with an amusing cautionary tale which illustrates the type of blunder that can still appear in the pages of a refereed journal (1975) when scientists (in this

case physicists) attempt to deduce the structure of a compound by spectroscopic techniques alone, without ever analysing the substance being investigated. The work<sup>(160)</sup> purported to establish the presence of a new molecule  $\text{Cl}_3\text{SI}$  in solid solution with an ionic complex  $[\text{SCl}_3]^+[\text{ICl}_2]^-$ , thus leading to an overall formula for the crystals of  $\text{S}_2\text{Cl}_8\text{I}_2$ . The mixed compound had apparently been made originally by M. Jaillard in 1860: he obtained it as beautiful transparent yellow-orange prismatic crystals by treating a mixture of sulfur and iodine with a stream of dry  $\text{Cl}_2$ . R. Weber obtained the same material in 1866 by passing  $\text{Cl}_2$  into a solution of  $\text{I}_2$  in  $\text{CS}_2$  but he reported a composition of  $\text{S}_2\text{Cl}_7\text{I}$  rather than Jaillard's  $\text{SCl}_4\text{I}$  ( $\text{S}_2\text{Cl}_8\text{I}_2$ ). The implausibility of forming a stable compound containing an S–I bond in this way, coupled with the perceptive recognition that the published Raman spectrum had bands that could be assigned to  $[\text{ICl}_4]^-$  rather than  $[\text{ICl}_2]^-$ , led P. N. Gates and A. Finch to reinvestigate the compound.<sup>(161)</sup> It transpired that the nineteenth-century workers had used  $\text{S}=16$  as the atomic weight of sulfur so the true chemical composition of the crystals was, in fact,  $\text{SCl}_7\text{I}$ . The previous spectroscopic interpretation<sup>(160)</sup> was therefore totally incorrect and the compound was shown to be  $[\text{SCl}_3]^+[\text{ICl}_4]^-$ . This was later confirmed by a single-crystal X-ray diffraction study (p. 691).<sup>(149)</sup> In short, far from containing the new iodo-derivative  $\text{Cl}_3\text{SI}$ , the compound did not even contain an S–I bond.

### 15.2.4 Oxohalides of sulfur

Sulfur forms two main series of oxohalides, the thionyl dihalides  $\text{OS}^{\text{IV}}\text{X}_2$  and the sulfuryl dihalides  $\text{O}_2\text{S}^{\text{VI}}\text{X}_2$ . In addition, various other oxofluorides and peroxofluorides are known (p. 688). Thionyl fluorides and chlorides are colourless volatile liquids (Table 15.14);  $\text{OSBr}_2$  is rather less volatile and is orange-coloured.

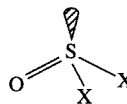
<sup>158</sup> G. A. BOWMAKER and D. A. ROGERS, *J. Chem. Soc., Dalton Trans.*, 1146–51 (1981).

<sup>159</sup> R. MINKWITZ and H. PRENZEL, *Z. anorg. allg. Chem.* **548**, 91–102 (1987).

<sup>160</sup> Y. TAVARES-FORNERIS and R. FORNERIS, *J. Mol. Structure* **24**, 205–13 (1975).

<sup>161</sup> A. FINCH, P. N. GATES and T. H. PAGE, *Inorg. Chim. Acta* **25**, L49–L50 (1977).

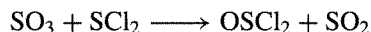
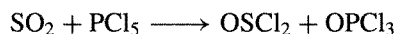
Table 15.14 Some properties of thionyl dihalides,



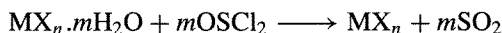
Property	OSF <sub>2</sub>	OSFCl	OSCl <sub>2</sub>	OSBr <sub>2</sub>
MP/°C	-110	-120	-101	-50
BP/°C	-44	12	76	140
<i>d</i> (O-S)/pm	141.2	—	145	145 (assumed)
<i>d</i> (S-X)/pm	158.5	—	207	227
angle O-S-X	106.8°	—	106°	108°
angle X-S-X	92.8°	—	114°(?)	96°

All have pyramidal molecules (*C<sub>s</sub>* point group for OSX<sub>2</sub>), and OSFCl is chiral though stereochemically labile. Dimensions are in Table 15.14; the short O-S distance is notable. The unstable compound OSI<sub>2</sub> was mentioned on p. 692.

The most important thionyl compound is OSCI<sub>2</sub> — it is readily prepared by chlorination of SO<sub>2</sub> with PCl<sub>5</sub> or, on an industrial scale, by oxygen-atom transfer from SO<sub>3</sub> to SCl<sub>2</sub>:



OSCl<sub>2</sub> reacts vigorously with water and is particularly valuable for drying or dehydrating readily hydrolysable inorganic halides:

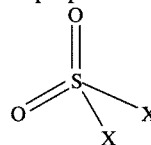


Examples are MgCl<sub>2</sub>·6H<sub>2</sub>O, AlCl<sub>3</sub>·6H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O, etc. Thionyl chloride begins to decompose above its bp (76°) into S<sub>2</sub>Cl<sub>2</sub>, SO<sub>2</sub>, and Cl<sub>2</sub>; it is therefore much used as an oxidizing and chlorinating agent in organic chemistry. Fluorination with SbF<sub>3</sub>/SbF<sub>5</sub> gives OSF<sub>2</sub>; use of NaF/MeCN gives OSFCl or OSF<sub>2</sub> according to conditions. Thionyl chloride also finds some use as a nonaqueous ionizing solvent as does SO<sub>2</sub> (p. 700) and the formally related dimethylsulfoxide (dmsO), Me<sub>2</sub>SO (mp 18.6°, bp 189°, viscosity  $\eta_{25}$  1.996 centipoise, dielectric constant  $\epsilon_{25}$  46.7). OSF<sub>2</sub> is a useful low-temperature fluorinating agent in organic chemistry: it converts active C-H and P-H

groups into C-F and P-F, and replaces N-H with N-S(O)F.<sup>(162)</sup>

Sulfuryl halides, like their thionyl analogues, are also reactive, colourless, volatile liquids or gases (Table 15.15). The most important compound is O<sub>2</sub>SCL<sub>2</sub>, which is made on an industrial scale by direct chlorination of SO<sub>2</sub> in the presence of a catalyst such as activated charcoal (p. 274) or FeCl<sub>3</sub>. It is stable to 300° but begins to dissociate into SO<sub>2</sub> and Cl<sub>2</sub> above this: it is a useful reagent for introducing Cl or O<sub>2</sub>SCL into organic compounds. O<sub>2</sub>SCL<sub>2</sub> can be regarded as the acid chloride of H<sub>2</sub>SO<sub>4</sub> and, accordingly, slow hydrolysis (or ammonolysis) yields O<sub>2</sub>S(OH)<sub>2</sub> or O<sub>2</sub>S(NH<sub>2</sub>)<sub>2</sub>. Fluorination yields O<sub>2</sub>SF<sub>2</sub> (also prepared by SO<sub>2</sub> + F<sub>2</sub>) and comproportionation of this with O<sub>2</sub>SCL<sub>2</sub> and O<sub>2</sub>SBr<sub>2</sub> yield the corresponding O<sub>2</sub>SFX species.

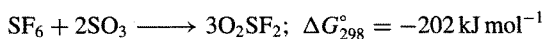
Table 15.15 Some properties of sulfuryl dihalides,



Property	O <sub>2</sub> SF <sub>2</sub>	O <sub>2</sub> SFCl	O <sub>2</sub> SCL <sub>2</sub>	O <sub>2</sub> SFBr
MP/°C	-120	-125	-54	-86
BP/°C	-55	7	69	41
<i>d</i> (O-S)/pm	140.5	—	143	—
<i>d</i> (S-X)/pm	153.0	—	199	—
angle O-S-O	124°	—	120°	—
angle X-S-X	96°	—	111°	—

<sup>162</sup>T. MAHMOOD and J. M. SHREEVE, *Inorg. Chem.* **24**, 1395-8 (1985).

All these compounds have (distorted) tetrahedral molecules, those of formula  $O_2SX_2$  having  $C_{2v}$  symmetry and the others  $C_s$ . Dimensions are in Table 15.15: the remarkably short O–S and S–F distances in  $O_2SF_2$  should be noted (cf. above). Indeed, the implied strength of bonding in this molecule is reflected by the fact that it can be made by reacting the normally extremely inert compound  $SF_6$  (p. 687) with the fluoro-acceptor  $SO_3$ :



A 20% conversion can be effected by heating the two compounds at  $250^\circ$  for 24 h.

### 15.2.5 Oxides of sulfur

At least thirteen proven oxides of sulfur are known to exist<sup>(163)</sup> though this profusion should not obscure the fact that  $SO_2$  and  $SO_3$  remain by far the most stable and unquestionably the most important economically. The six homocyclic polysulfur monoxides  $S_nO$  ( $5 < n < 10$ ) are made by oxidizing the appropriate *cyclo-S<sub>n</sub>* (p. 656) with trifluoroperoxoacetic acid,  $CF_3C(O)OOH$ , at  $-30^\circ$ . The dioxides  $S_7O_2$  and  $S_6O_2$  are also known. In addition there are the thermally unstable acyclic oxides  $S_2O$ ,  $S_2O_2$ ,  $SO$  and the fugitive species  $SOO$  and  $SO_4$ . Several other compounds were described in the older literature (pre-1950s) but these reports are now known to be in error. For example, the blue substance of composition “ $S_2O_3$ ” prepared from liquid  $SO_3$  and sulfur now appears to be a mixture of salts of the cations  $S_4^{2+}$  and  $S_8^{2+}$  (p. 664) with polysulfate anions. Likewise a “sulfur monoxide” prepared by P. W. Schenk in 1933 was shown by D. J. Meschi and R. J. Meyers in 1956 to be a mixture of  $S_2O$  and  $SO_2$ . The well-established lower oxides of S will be briefly reviewed before  $SO_2$  and  $SO_3$  are discussed in more detail.

#### Lower oxides<sup>(163)</sup>

Elegant work by R. Steudel and his group in Berlin has shown that, when *cyclo-S<sub>10</sub>*, *-S<sub>9</sub>*, and *-S<sub>8</sub>* are dissolved in  $CS_2$  and oxidized by freshly prepared  $CF_3C(O)O_2H$  at temperatures below  $-10^\circ$ , modest yields (10–20%) of the corresponding crystalline monoxides  $S_nO$  are obtained. Similar oxidation of *cyclo-S<sub>7</sub>*, and  $\alpha$ - and  $\beta$ - $S_6$  in  $CH_2Cl_2$  solution yields crystalline  $S_7O$ ,  $S_7O_2$ , and  $\alpha$ - and  $\beta$ - $S_6O$ . Crystals of  $S_6O_2$  and  $S_5O$  ( $d > -50^\circ$ ) have not yet been isolated but the compounds have been made in solution by the same technique.  $S_8O$  had previously been made (1972) by the reaction of  $OSCl_2$  and  $H_2S_7$  in  $CS_2$  at  $-40^\circ$ : it is one of the most stable compounds in the series and melts (with decomposition) at  $78^\circ$ . All the compounds are orange or dark yellow and decompose with liberation of  $SO_2$  and sulfur when warmed to room temperature or slightly above. Structures are in Fig. 15.24. It will be noted that  $S_7O$  is isoelectronic and isostructural with  $[S_7I]^+$  (p. 692). This invites the question as to whether  $S_7S$  can be prepared as a new structural isomer of *cyclo-S<sub>8</sub>*.

$S_8O$  reacts with  $SbCl_5$  in  $CS_2$  over a period of 9 days at  $-50^\circ$  to give a 71% yield of the unstable orange adduct  $S_8O.SbCl_5$ <sup>(164)</sup> its structure and dimensions are in Fig. 15.25a. It will be noted that the  $S_8O$  unit differs from molecular  $S_8O$  in having an equatorially bonded O atom and significantly different S–O and S–S interatomic distances. The X-ray crystal structure was determined at  $-100^\circ C$  as the adduct decomposes within 5 min at  $25^\circ$  to give  $OSCl_2$ ,  $SbCl_3$  and  $S_8$ . When a similar reaction was attempted with  $\beta$ - $S_6O$ , the novel dimer  $S_{12}O_2.2SbCl_5.3CS_2$  was obtained as orange crystals in 10% yield after 1 week at  $-50^\circ$ <sup>(165)</sup> (Fig. 15.25b). Formation of the centrosymmetric  $S_{12}O_2$  molecule, which is still unknown in the uncoordinated state, can be

<sup>164</sup> R. STEUDEL, T. SANDOW and J. STEIDEL, *J. Chem. Soc., Chem. Commun.*, 180–1 (1980).

<sup>165</sup> R. STEUDEL, J. STEIDEL and J. PICKARDT, *Angew. Chem. Int. Edn. Engl.* **19**, 325–6 (1980).

<sup>163</sup> *Gmelin Handbuch der Anorganischen Chemie*, 8th edn., Schwefel Oxide, Ergänzungsband 3, 1980, 344 pp.