SULFUR COMPOUNDS

1. Introduction

1.1. Carbon Sulfides. The only commercial carbon sulfide is carbon disulfide (qv) [75-15-0], CS_2, which is covered in a separate article. There are several unstable carbon sulfides. Carbon subsulfide [12976-57-2], C_3S_2, is a red liquid [mp −0.5°C, bp 60−70°C at 1.6 kPa (12 mmHg)] produced by the action of an electric arc on carbon disulfide (1–4). The structure has been shown to be S=C=C=C=S. It is unstable and decomposes in a few weeks at room temperature. It decomposes explosively when heated rapidly (5,6). Dilute solutions in CS_2 are fairly stable, but photochemical polymerization to $(C_3S_2)_x$ occurs.

Carbon monosulfide [2944-05-0], CS, is an unstable gas produced by the decomposition of carbon disulfide at low pressure in a silent electrical discharge or photolytically (1–3). It decomposes with a half-life of seconds or minutes to a black solid of uncertain composition (1–3). Stable coordination complexes of CS with metals have been prepared by indirect means (7). A review of the synthetic utility of CS has been published (8).

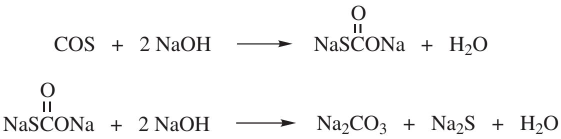
1.2. Incompletely Characterized Carbon Sulfides. A poorly characterized black solid, known as carsul, occurs as a residue in sulfur distillation or as a precipitate in molten Frasch sulfur (9,10). Although this material may approach the composition of a carbon sulfide, it is more likely also to contain some chemically bound hydrogen and possibly other elements. Carbon−sulfur surface compounds of the formula C_xS, where x is > 4, are prepared by reaction of carbonaceous materials with a sulfur-containing gas, eg, sulfur dioxide at 400−700°C. They are useful as cathodes in electrical cells (11). Other poorly characterized, thermally stable black solids with sulfur contents ranging as high as 46 wt% have been reported as products of high temperature reactions of sulfur with charcoal, cellulose, and various carbon compounds (12,13).

1.3. Carbonyl Sulfide. *Physical Properties.* Carbonyl sulfide [463-58-1] (carbon oxysulfide), COS, is a flammable colorless gas that is odorless when pure; however, it has been described as having a foul odor. Physical constants and thermodynamic properties are listed in Table 1 (14,15). Further data are given in recent reviews of COS (16,17). The vapor pressure has been fitted to an equation, and a detailed study has been made of the phase equilibria of the carbonyl sulfide−propane system, which is important in the purification of propane fuel (18,19). Carbonyl sulfide can be adsorbed on molecular sieves (qv) as a means for removal from propane (20). This approach has been compared to the use of various solvents and reagents (21).

Chemical Properties. Reviews of carbonyl sulfide chemistry are available (15,16,22). The 2002 review (17) is especially thorough. Carbonyl sulfide is a stable compound and can be stored under pressure in steel cylinders as compressed gas in equilibrium with liquid. At ∼600°C carbonyl sulfide disproportionates to carbon dioxide and carbon disulfide; at ∼900°C it dissociates to carbon monoxide and sulfur. It burns with a blue flame to carbon dioxide and sulfur dioxide. Carbonyl sulfide reacts slowly with water to form carbon dioxide and hydrogen sulfide. Much technology has been developed for hydrolysis of carbonyl sulfide in gas streams to permit the more ready removal of the sulfur content as hydrogen sulfide. Shift-catalyst methodology has been developed for reducing the amount of COS formed in the Claus process for recovering sulfur from hydrogen sulfide (23,24). The commercial processes for hydrolyzing COS have been reviewed in detail (17,25).

Alternative means for removal of carbonyl sulfide for gas streams involve hydrogenation. For example, the Beavon and Scot processes for removal of sulfur compounds remaining in Claus unit tail gases involves hydrolysis and hydrogenation over cobalt molybdate catalyst resulting in the conversion of carbonyl sulfide, carbon disulfide, and other sulfur compounds to hydrogen sulfide (25).

Carbonyl sulfide reacts slowly with aqueous alkali metal hydroxides, which can therefore be used to free carbonyl sulfide from acidic gases. The half-life at pH 12 (0.01 *N* KOH) is 3 min at 22°C. The product initially formed from carbonyl sulfide and alkali is the thiocarbonate [534-18-9], which then breaks down to carbonate and sulfide:



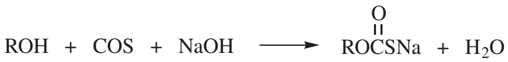
$$\mathrm{COS} + 2\,\mathrm{NaOH} \longrightarrow \mathrm{NaS}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{ONa} + \mathrm{H_2O}$$

$$\mathrm{NaS}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{ONa} + 2\,\mathrm{NaOH} \longrightarrow \mathrm{Na_2CO_3} + \mathrm{Na_2S} + \mathrm{H_2O}$$

To effectively remove carbonyl sulfide from a gas stream, special alkaline scrubbing liquors are used. These contain sodium aluminate or sodium plumbite, or they are made of alkalies with a hydrolysis catalyst based on Zn, Fe, Ni, or Cu. Diethanolamine, diglycolamine, or other alkanolamines (qv) mixed with water remove carbonyl sulfide from sour, ie, acid–gas-containing, gas streams (25,26) (see Carbon dioxide).

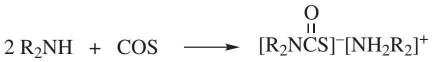
Carbonyl sulfide reacts with chlorine forming phosgene (qv) and sulfur dichloride [10545-99-0], and with ammonia forming urea and ammonium sulfide [12135-76-1]. Carbonyl sulfide attacks metals, eg, copper, in the presence of moisture and is thought to be involved in atmospheric sulfur corrosion (27,28). This process may involve initial oxidation of carbonyl sulfide to sulfur and subsequent corrosion of copper by sulfur. The presence of carbonyl sulfide in propane gas at levels above a few ppm may cause the gas to fail the copper-corrosion test.

It reacts with alcohols in the presence of base to form monothiocarbonate esters:



$$\mathrm{ROH} + \mathrm{COS} + \mathrm{NaOH} \longrightarrow \mathrm{RO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{SNa} + \mathrm{H_2O}$$

Carbonyl sulfide reacts with amines to form thiocarbamates:



$$2\,\mathrm{R_2NH} + \mathrm{COS} \longrightarrow [\mathrm{R_2N}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{S}]^{-}[\mathrm{NH_2R_2}]^{+}$$

With amines, such as those used in gas sweetening, it reacts forming mainly ureas:

$$\mathrm{COS} + 2\,\mathrm{HOCH_2CH_2OCH_2CH_2NH_2} \longrightarrow \mathrm{(HOCH_2CH_2OCH_2CH_2NH)_2CO} + \mathrm{H_2S}$$

The kinetics of reaction of COS with aqueous amines have been studied (29).

The photolysis of carbonyl sulfide is a laboratory method for the production of monoatomic sulfur, a short-lived species (30).

Occurrence and Preparation. Carbonyl sulfide is formed by many high temperature reactions of carbon compounds with donors of oxygen and sulfur. Usually, as forming COS as a byproduct, the principal route is the following reaction (31):

$$\mathrm{CO} + \mathrm{S}^0 \rightleftharpoons \mathrm{COS}$$

This equilibrium favors COS up to ~500°C. At higher temperatures, COS dissociates increasingly, eg, to 64% at 900°C. The reaction may be run at 65–200°C to produce carbonyl sulfide if an alkaline catalyst is used (32). A Rhodia patent describes the manufacture of carbonyl sulfide by the reaction of methanol with sulfur at 500–800°C (33). However, the preferred route both for laboratory and commercial production is the reaction of either alkali metal thiocyanate or ammonium thiocyanate with strong (~50%) sulfuric acid:

$$\mathrm{NH_4SCN} + 2\,\mathrm{H_2SO_4} + \mathrm{H_2O} \longrightarrow 2\,\mathrm{NH_4HSO_4} + \mathrm{COS}$$

To make pure COS, the evolved gas that may contain CO_2, SO_2, H_2S, CS_2, HCHO, and HCN as byproducts, is scrubbed with copper sulfate solution, alkali solution, ethanolic aniline, and concentrated sulfuric acid. This thiocyanate route is believed to have been commercially practiced to make COS for large-scale thiocarbamate herbicide production.

Other important reactions yielding carbonyl sulfide follow (34,35):

Reaction	Remarks
$CO_2 + H_2S \rightarrow COS + H_2O$	in Claus furnace and over various catalysts
$CO_2 + CS_2 \rightleftharpoons 2\,COS$	at ~500°C, catalyzed by silica
$CS_2 + SO_2 \rightarrow COS + SO_2 + S^0$	>400°C as gases, at low temperatures as liquids
$HSCN + H_2O \rightarrow COS + NH_3$	in H_2SO_4 at 20°C
$FeS_2 + CO \rightarrow FeS + COS$	fast >800°C

Carbonyl sulfide occurs as a by-product in the manufacture of carbon disulfide and is an impurity in some natural gases, in many manufactured fuel gases and refinery gases, and in combustion products of sulfur-containing fuels (25). It tends to be concentrated in the propane fraction in gas fractionation; an amine sweetening process is needed to remove it. The kinetics of its hydrolysis in connection with the propane "sweetening" process have been studied in detail (36). The mechanisms that lead to carbonyl sulfide as a by-product in the Claus process for sulfur recovery (37) have been studied.

Carbonyl sulfide is overall the most abundant sulfur-bearing compound in the earth's atmosphere: 430–570 parts per trillion (10^{12}), although it is exceeded by H_2S and SO_2 in some industrial urban atmospheres (27). It is also found in the stratosphere (38). Carbonyl sulfide is believed to originate from microbes, volcanoes, and the burning of vegetation, as well as from industrial processes. It may be the main cause of atmospheric sulfur corrosion (39). A mass budget study was done on COS and other sulfur compounds in the atmosphere (40). The photochemical and nonphotochemical formation and destruction of COS in the ocean has been studied (40–42) as has the uptake of COS in the soil (43), in marine algae (44), and in higher plants (45).

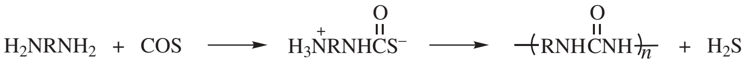
Production, Shipment, and Specifications. Total industrial production figures were not found. Captive production from thiocyanate salts for thiolcarbamate herbicide synthesis may be substantial. Carbonyl sulfide is available in 97% min purity in cylinders up to 31.8 kg contained weight. It is shipped as a flammable gas. There appears to be no full-scale merchant production of carbonyl sulfide in the United States.

Analytical Methods. Detection of carbonyl sulfide in air can be done by gas chromatography (gc) or by combustion to sulfur dioxide and determination of the latter. Where hydrogen sulfide and carbonyl sulfide occur together, the carbonyl sulfide can be determined by combustion after hydrogen sulfide is absorbed by lead acetate, which does not absorb carbonyl sulfide (46). The ASTM copper strip test for sulfur compounds in propane does not give a reliable response for COS (47).

Health and Safety Factors. Carbonyl sulfide is dangerously poisonous, more so because it is practically odorless when pure. It is lethal to rats at 2900 ppm. Studies show an LD_{50} (rat, ip) of 22.5 mg/kg. The mechanism of toxic action appears to involve breakdown to hydrogen sulfide (36). It acts principally on the central nervous system with death resulting mainly from respiratory paralysis. Little is known regarding the health effects of subacute or chronic exposure to carbonyl sulfide; a 400-$\mu g/m^3$ max level has been suggested until more data are available (48). Carbon oxysulfide has a reported inhalation toxicity in mice LD_{50} (mouse) = 2900 ppm (49).

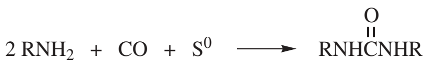
Uses. There may be captive use of carbonyl sulfide for production of certain thiocarbamate herbicides (qv). One patent (50) describes the reaction of diethylamine with carbonyl sulfide to form a thiocarbamate salt that is then alkylated with 4-chlorobenzyl halide to produce *S*-(4-chlorobenzyl) *N,N*-diethylthiocarbamate [28249-77-6], ie, thiobencarb herbicide [28249-77-6], with 2,3-dichloroallyl chloride to produce diallate herbicide [2304-16-4] and with 2,3,3-trichloroallyl chloride to produce triallate herbicide [2303-17-5]. Carbonyl sulfide is also reported to be useful for the preparation of aliphatic polyureas. In these preparations, potassium thiocyanate and sulfuric acid are used to first generate carbonyl sulfide, COS, which then reacts with a diamine:

$$2\,KCNS + 2\,H_2SO_4 + 2\,H_2O \longrightarrow 2\,COS + (NH_4)_2SO_4 + K_2SO_4$$



$$H_2NRNH_2 + COS \longrightarrow H_3\overset{+}{N}RNH\overset{\overset{O}{\|}}{C}S^- \longrightarrow -\!\left(RNH\overset{\overset{O}{\|}}{C}NH \right)_{\!n}\!- + H_2S$$

Monoureas can also be prepared using COS and an alkylamine, or an arylamine in the absence or presence of a catalyst, where R = H, alkyl, or aryl (51):



$$2\,RNH_2 + CO + S^0 \longrightarrow RNH\overset{\overset{O}{\|}}{C}NHR$$

The above reaction produces COS as an intermediate, which can be isolated when a catalytic amount of selenium is present (52).

COS shows promise as a stored product fumigant, as an alternative to methyl bromide or phosphine. It is effective in killing insects, mites (53), and fungi (54).

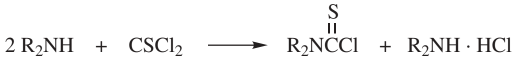
2. Thiophosgene

2.1. Physical Properties. Thiophosgene [463-71-8] (thiocarbonyl chloride), $CSCl_2$, is a malodorous, red-yellow liquid (bp 73.5°C, $d^{15}{}_{20}$ 1.509, $n^{20}{}_D$ 1.5442). It is only slightly soluble with decomposition in water, but it is soluble in ether and various organic solvents.

2.2. Chemical Properties. Thiophosgene is more resistant to hydrolysis than its oxygen analogue, phosgene, but it is slowly hydrolyzed to carbon dioxide, hydrogen sulfide, and hydrochloric acid. It can be oxidized to a lacrimatory thiophosgene *S*-oxide (55). Its utility in organic synthesis has been reviewed (56,57). Its photochemical properties have been studied and reviewed (58).

Thiophosgene reacts with alcohols and phenols to form chlorothionoformates or thiocarbonates. The most studied reactions of thiophosgene are with primary amines to give isothiocyanates and with secondary amines to give thiocarbamyl chlorides:

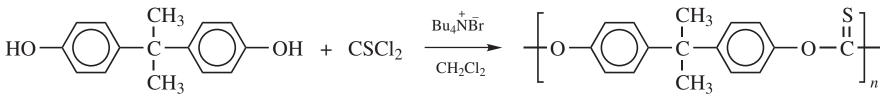
$$RNH_2 + CSCl_2 \longrightarrow RN{=}C{=}S + 2\,HCl$$



$$2\,R_2NH + CSCl_2 \longrightarrow R_2N\overset{\overset{S}{\|}}{C}Cl + R_2NH \cdot HCl$$

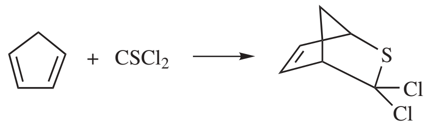
Because of the toxicity of thiophosgene, alternative methods for making organic isothiocyanates have been developed (59).

The reaction of thiophosgene with various bisphenols using phase-transfer catalysis gives polythiocarbonates (60):



Most of the reactions of thiophosgene involve the expected chemistry of an acid chloride, in which the chlorine atoms are replaceable by various nucleophiles. A typical reaction is with *N*-alkyldiacylhydrazine to form a 1,3,4-oxadiazoline-5-thione, with agrochemical utility (61).

A reaction involving the C=S bond is the Diels–Alder addition:



The reaction of thiophosgene with potassium fluoride or other fluoride salts provides trifluoromethanethiolate, useful for the preparation of trifluoromethyl sulfides of pharmaceutical and agrochemical utility (62,63).

2.3. Preparation and Uses. Thiophosgene forms from the reaction of carbon tetrachloride with hydrogen sulfide, sulfur, or various sulfides at elevated temperatures. Of more preparative value is the reduction of trichloromethanesulfenyl chloride [594-42-3] by various reducing agents, eg, tin and hydrochloric acid, stannous chloride, iron and acetic acid, phosphorus, copper, sulfur dioxide with iodine catalyst, or hydrogen sulfide over charcoal or silica gel catalyst (56,57).

There may be no full-scale U.S. commercial production of thiophosgene, but it is available in glass ampules from laboratory reagent suppliers. Thiophosgene may be produced overseas as an intermediate for tolnaftate (2-naphthyl *N*-methyl-*N*-*m*-tolylthiocarbamate) [2398-96-1], an important antifungal drug.

2.4. Health and Safety Factors. Thiophosgene has an LD_{50} (rat, oral) of 929 mg/kg and an LC_{50} (inhalation, rat) of 370 mg/m^3 (64). It has both irritant and systemic toxic properties. It is believed to have been used or tried as a poison gas in World War I.

The MSDS (65) for thiophosgene describes it as a highly toxic, corrosive, lachrymatory and moisture sensitive compound. It may be fatal if inhaled, swallowed, or absorbed through the skin. When using this material one should wear the appropriate NIOSH/OSHA-approved respirator, chemical-resistant gloves, safety goggles, and other protective clothing. It should be used only in a chemical fume hood.

3. Trichloromethanesulfenyl Chloride

3.1. Physical Properties. Trichloromethanesulfenyl chloride [594-42-3] (perchloromethyl mercaptan, a misnomer but used as the common commercial name), CCl_3SCl, is a strongly acrid, pale yellow liquid, boiling at 149°C with some decomposition at atmospheric pressure, 68°C at 6.93 kPa (52 mmHg), and 25°C at 0.8 kPa (6 mmHg); sp. gr. (20°C/4°C) 1.6996; $n^{23}{}_D$ 1.541 (66,67). It slowly hydrolyzes and is soluble in most organic solvents. It has a vapor density of 6.414 (air = 1) and a vapor pressure of 3.0 mmHg at 20°C (68,69). It is insoluble in water, and is nonflammable but supports combustion (68).

3.2. Chemical Properties. A detailed review of the chemistry of trichloromethanesulfenyl chloride has been published (70). It is stable for prolonged periods at ambient temperature, but decomposes slowly at its atmospheric boiling point forming sulfur monochloride, carbon tetrachloride, carbon disulfide, and polymeric oils. Storage in contact with iron causes it to decompose to carbon tetrachloride and sulfur monochloride. It is hydrolyzed only slowly by water at room temperature in a complex series of steps, proceeding by way of the unstable sulfenic acid and an isolable thiophosgene *S*-oxide [24768-49-8], $Cl_2C{=}S{=}O$, yielding a complex product mixture including hydrochloric acid, phosgene, thiophosgene, trichloromethanesulfonyl chloride, chlorocarbonylsulfenyl chloride [2757-23-5], and bis(trichloromethyl) disulfide [15110-08-4] (71). At 160°C, hydrolysis is rapid and leads ultimately to the formation of carbon dioxide, hydrochloric acid, and sulfur. Trichloromethanesulfenyl chloride reacts rapidly with sodium hydroxide forming sodium dichloromethanesulfinate [36829-83-1], $CHCl_2SO_2Na$ (72).

The oxidation of trichloromethanesulfenyl chloride by nitric acid or oxidative chlorination in the presence of water yields trichloromethanesulfonyl chloride [2547-61-7], CCl_3SO_2Cl, which is a lacrimatory solid (mp 140–142.5°C), which is surprisingly stable to hydrolysis and can be steam distilled. Trichloromethanesulfenyl chloride can be reduced to thiophosgene by metals in the presence of acid and by various other reducing agents. The sulfur-bonded chlorine of trichloromethanesulfenyl chloride is most easily displaced by nucleophilic reagents, but under some conditions, the carbon-bound chlorines are also reactive (73).

$$\mathrm{CCl_3SCl + 2\,RNH_2 \longrightarrow CCl_3SNHR + RNH_2\cdot HCl}$$

$$\mathrm{CCl_3SCl + RONa \longrightarrow CCl_3SOR + NaCl}$$

$$\mathrm{CCl_3SCl + RSH \longrightarrow CCl_3SSR + HCl}$$

$$\mathrm{CCl_3SCl + C_6H_5N\,(CH_3)_2 \longrightarrow \mathit{p}\text{-}CCl_3SC_6H_4N\,(CH_3)_2\cdot HCl}$$

$$\mathrm{CCl_3SCl + 4\,RONa \longrightarrow (RO)_4C + 4\,NaCl + S^0}$$

$$\mathrm{CCl_3SCl + KF \longrightarrow CFCl_2SCl + KCl}$$

Trichloromethanesulfenyl chloride can be added across double bonds under either free-radical or cationic-initiated conditions (74,75):

$$\mathrm{CCl_3SCl + R_2C{=}CR_2 \longrightarrow CCl_3SCR_2CClR_2}$$

Aryl chlorothioformates are prepared, eg, by reaction of a mixture of 3-$(CH_3)_3CC_6H_4OH$ and $NaHSO_3$, CCl_3SCl, KI, and concentrated H_2SO_4 in CCl_4 plus H_2O for 10 h at room temperature to give a 63% yield of $(CH_3)_3CC_6H_4OCSCl$ (76). Phenylthiocarbamoyl chlorides are useful as intermediates for pharmaceuticals and agrochemicals were prepared by the reaction of CCl_3SCl with aromatic amines (77).

3.3. Manufacture. Trichloromethanesulfenyl chloride is made commercially by chlorination of carbon disulfide with the exclusion of iron or other metals, which catalyze the chlorinolysis of the C–S bond to produce carbon tetrachloride and sulfur chloride by-products that are disposal problems. Various catalysts, notably iodine and activated carbon, are effective. The product is purified by fractional distillation to a minimum purity of 95%. Continuous processes have been described wherein carbon disulfide chlorination takes place on a granular charcoal column (78,79). A series of patents describes means for yield improvement by chlorination in the presence of difunctional carbonyl compounds, phosphonates, phosphonites, phosphites, phosphates, or lead acetate (80). Chlorination in the presence of aqueous hydrochloric and sulfuric acid is reported in an Olin patent (81) to give higher conversion to trichloromethanesulfenyl chloride with only carbon tetrachloride as by-product, and is believed to be commercially practiced overseas.

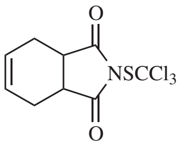
3.4. Shipment and Storage. Much or perhaps all of the trichloromethanesulfenyl chloride produced is used captively. However, it can be shipped in nickel, Monel, or glass.

3.5. Economic Aspects. The U.S. manufacture of trichloromethanesulfenyl chloride was carried out by Zeneca, Inc. (Perry, Ohio), but is believed to be discontinued. Production is probable in Israel and India for captive use in production of captan and folpet fungicides.

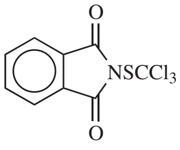
3.6. Analytical Methods. A method has been described for gc analysis of trichloromethanesulfenyl chloride as well as of other volatile sulfur compounds (82). A method has been recommended for determining small amounts of trichloromethanesulfenyl chloride in air or water on the basis of a color-forming reaction with resorcinol (83).

3.7. Health and Safety Factors. Trichloromethanesulfenyl chloride is extremely toxic and mutagenic (84). It has an LD_{50} in rabbits (percutaneous) of 1410 mg/kg (85,86) and an LC_{50} in rats (male) of 11 ppm/h (86). The LD_{50} oral in rats is 83 mg/kg (64). There are hazards involved from inhalation and possible skin contact. Severe local irritation can result from contact of the liquid or vapor with the skin, eyes, mucous membranes, and upper respiratory tract. The irritating nature of the vapor may also serve as a warning of its presence. The MSDS should be consulted and all work carried out with good ventilation in a laboratory fume hood with the operator wearing proper gloves, suitable protective clothing, and respiratory equipment. The TLV of trichloromethanesulfenyl chloride is an 8-h time-weighted average exposure of 0.1 ppm (0.8 mg/m^3).

3.8. Uses. The principal commercial application for trichloromethanesulfenyl chloride is as an intermediate for the manufacture of fungicides, the most important being captan [*N*-(trichloromethylthio)4-cyclohexene-1,2-dicarboximide] [133-06-2] (**1**) and folpet [*N*-(trichloromethylthio)phthalimide] [133-07-3] (**2**) (see Fungicides, agricultural):



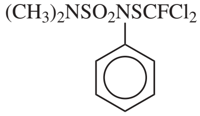
(1)



(2)

A commercial soil or seed treatment fungicide, 5-ethoxy-3-trichloromethyl-1,2,4-thiadiazole [2593-15-9] (etridiazole) is prepared from 2-chloro-3-trichloromethyl-1,2,4-thiadiazole [5848-93-1], a product of trichloromethanesulfenyl chloride and trichloroacetamidine (87).

A fluorinated analogue, $CFCl_2SCl$, is made in Europe from trichloromethanesulfenyl chloride and is used for production of the fungicide dichlorofluanid [085-98-9] (**3**) and tolylfluanid [731-27-1] (**4**) (88):



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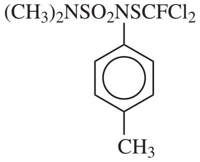
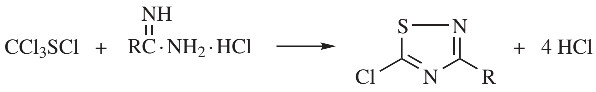


(4)

Trichloromethanesulfenyl chloride has also been used for the preparation of lubricant additives (see LUBRICATION AND LUBRICANTS). Some higher homologues and analogues of trichloromethanesulfenyl chloride have been reported, ie, trichlorovinylsulfenyl chloride [19411-15-5], 1,1,2,2-tetrachloroethanesulfenyl chloride [1185-09-7], 1,2,2,2-tetrachloroethanesulfenyl chloride [920-62-7], and pentachloroethanesulfenyl chloride [5940-94-3] (89–93). A commercial fungicide, Captafol [2425-06-1], is the reaction product of 1,1,2,2-tetrachloroethanesulfenyl chloride with tetrahydrophthalimide (94).

Trichloromethanesulfenyl chloride is useful in the preparation of various series of sulfur-containing heterocycles. A commercially significant example is the preparation of 3-substituted-5-chloro-1,2,4-thiadiazoles.



4. Hydrogen Sulfide

Hydrogen sulfide [7783-06-4] is present in the gases from many volcanoes, sulfur springs, undersea vents, swamps, and stagnant bodies of water. It has been detected in outer space. Bacterial reduction of sulfates and bacterial decomposition of proteins forms hydrogen sulfide. Endogenous production has been found in mammals (75). The role of hydrogen sulfide in the natural sulfur cycles has been described (95). Of great importance as a source of sulfur are the so-called sour gases, which occur in large amounts in several locations. The concentrations of hydrogen sulfide in these sour gases are as follows (97):

Location	H_2S, wt%
France (Elf Aquitaine, Lacq)	15.0–16.0
Germany (Varnhorn)	22.4
Canada (Harmattan, Alberta)	53.5
Canada (Bearberry, Alberta)	90.0
Canada (Panther River, Alberta)	70–80
United States (Smackover, Miss.)	25–45
Russia (Astrakhan)	22.5
People's Republic of China (Zhaolanzhuang)	60–90

Hydrogen sulfide is a by-product of many industrial operations, eg, coking and the hydrodesulfurization of crude oil and of coal. Hydrodesulfurization is increasing in importance as the use of high sulfur crude oil becomes increasingly necessary (see Petroleum, refinery processes). A large future source of hydrogen sulfide may result if coal and bitumen gasification attains commercial importance (see Coal conversion processes).

4.1. Physical Properties. Hydrogen sulfide, H_2S, is a colorless gas having a characteristic rotten-egg odor. The physical properties of hydrogen sulfide are given in Table 2.

Detailed studies of the hydrogen sulfide–nitrogen system (105–107) and those of the hydrogen sulfide–water system have been reviewed (104,108). At low temperatures and high pressure, hydrogen sulfide forms a crystalline hexahydrate [66230-40-8]. Hydrogen sulfide is soluble in certain polar organic solvents, notably methanol, acetone, propylene carbonate, sulfolane, tributyl phosphate, various glycols, and glycol ethers (25,109). *N*-Methylpyrrolidinone is an exceptionally good solvent, dissolving 49 mL/g at 20°C at atmospheric pressure. Hydrogen sulfide is less soluble in nonpolar solvents; eg, the solubility of hydrogen sulfide gas at 20°C is 8.9 mL/g in hexane and 16.6 mL/g in benzene (95). Hydrogen sulfide is very soluble in alkanolamines, which are used as scrubbing solvents for removal of hydrogen sulfide from gas streams (25,110–112). The dissolution of hydrogen sulfide in amines results in the formation of a salt, which generally dissociates upon heating. Detailed studies have been published on the systems hydrogen sulfide–ethanolamine, –diethanolamine, –Sulfinol (a mixture of alkanolamines, sulfolane, and water) and –diglycolamine (113–116) (see Sulfur removal and recovery).

Because of its low dielectric constant, liquid hydrogen sulfide is a poor solvent for ionic salts, eg, NaCl, but it does dissolve appreciable quantities of anhydrous $AlCl_3$, $ZnCl_2$, $FeCl_3$, PCl_3, $SiCl_4$, and SO_2. Liquid hydrogen sulfide or hydrogen sulfide-containing gases under pressure dissolve sulfur. At equilibrium H_2S pressure, the solubility of sulfur in liquid H_2S at -45, 0, and 40°C is 0.261, 0.566, and 0.920 wt%, respectively (117). The equilibria among H_2S_x, H_2S, and sulfur have been studied (118,119).

4.2. Chemical Properties. Although hydrogen sulfide is thermodynamically stable, it can dissociate at very high temperatures. The decomposition thermodynamics and kinetics have been reviewed and the equilibrium constant for the reaction has been determined (120–122). Superadiabatic decomposition of hydrogen sulfide has been proposed and studied as a useful method for production of hydrogen (123–125).

$$2\,H_2S \rightleftharpoons 2\,H_2 + S_2$$

Above $\sim$850°C, the experimental hydrogen yield agrees well with that calculated by thermodynamic studies and a decomposition enthalpy of 16 kJ/mol (3.8 kcal/mol) is obtained and is in close agreement with theory. Below 850°C, equilibrium occurs quite slowly without a catalyst. With silica as catalyst and, to a greater degree, with cobalt molybdate or sulfided platinum as catalyst, greater hydrogen production occurs at 450–850°C than is theoretically predicted on the basis of the above equation. For example, at 477°C, 3.6 wt% H_2 results at equilibrium over cobalt molybdate. These enhanced hydrogen yields are explained on the basis of the formation of sulfur species other than S_2 (121).

The dissociation of hydrogen sulfide has been proposed as a potential hydrogen source for refineries, which normally need hydrogen and have ample hydrogen sulfide. Progress has been made in processes involving transition-metal catalysts, eg, Mo, W, or Ru sulfides, and processes involving the shifting of the equilibrium by removal of the sulfur (119,126). In the presence of a specially designed photoelectrolytic catalyst, visible light cleaves hydrogen sulfide to hydrogen and sulfur (127).

Hydrogen sulfide is oxidized by a number of oxidizing agents, as shown in Table 3. The actual products formed, where alternatives are indicated, are functions of the quantity of oxidant as well as of reaction conditions.

Certain of the above reactions are of practical importance. Various means for the direct oxidation of hydrogen sulfide have been reviewed (128).

The oxidation of hydrogen sulfide in a flame is one means for producing the sulfur dioxide required for a sulfuric acid plant. Oxidation of hydrogen sulfide by sulfur dioxide is the basis of the Claus process for sulfur recovery (129,130).

This process is discussed also in another article (see SULFUR REMOVAL AND RECOVERY). The Claus reaction can also take place under milder conditions in the presence of water, which catalyzes the reaction. However, the oxidation of hydrogen sulfide by sulfur dioxide in water is a complex process leading to the formation of sulfur and polythionic acids, the mixture known as Wackenroeder's liquid (131). The Claus process, which takes place in the vapor phase over heterogeneous catalysts, such as alumina or titania, and the conversion of the Claus process tail gas, are the subject of recent reviews (132–136). New selective and stable catalysts consisting of Fe_2O_3 on silicon carbide have been developed for the oxidation of H_2S in Claus tail gas (137).

By use of a short-contact reactor, the partial oxidation of hydrogen sulfide can be run to yield hydrogen, elemental sulfur, and water (138,139).

Oxidation of hydrosulfide salts to sulfur by water-soluble quinones is the basis of the Stretford and the Takahax processes used in sulfur recovery. Oxidation of hydrosulfide to sulfur by sodium vanadate, which can be regenerated by air, is a key reaction of the Beavon process, also used commercially in sulfur recovery. Oxidation of hydrogen sulfide until no odor is detectable proceeds with air over a cobalt molybdate catalyst (140). The reaction of hydrogen sulfide with I_2 is quantitative and is used for analytical determination of H_2S. The oxidation of hydrogen sulfide by hydrogen peroxide in aqueous sodium hydroxide is a means for abatement of hydrogen sulfide in steam from geothermal operations or steam condensate from power plants, sewage, and industrial waste systems (141) (see GEOTHERMAL ENERGY). Iron salts are effective catalysts for this reaction.

Anhydrous gaseous or liquid hydrogen sulfide is practically nonacidic, but aqueous solutions are weakly acid. The K_a for the first hydrogen is 9.1×10^{-8} at 18°C; for the second, is 1.2×10^{-15}. Reaction of hydrogen sulfide with one molar equivalent of sodium hydroxide gives sodium hydrosulfide; with two molar equivalents of sodium hydroxide, sodium sulfide forms. Hydrogen sulfide reacts with sodium carbonate to produce sodium hydrosulfide and sodium bicarbonate, a reaction that is reversible upon heating. Carbon dioxide can liberate hydrogen sulfide from sodium hydrosulfide. Various metal oxides and hydroxides react with hydrogen sulfide forming sulfides. A useful application is the removal of hydrogen sulfide by reaction with iron oxide (25):

$$Fe_2O_3\cdot H_2O + 3\,H_2S \longrightarrow Fe_2S_3 + 4\,H_2O$$

This reaction also yields some sulfur and ferrous products.

Anhydrous hydrogen sulfide does not react at ordinary temperatures with metals, eg, mercury, silver, or copper. However, in the presence of air and moisture, the reaction is rapid, leading to tarnishing in the case of silver and copper.

$$4\,Cu\ (\text{or } Ag) + 2\,H_2S + O_2 \longrightarrow 2\,Cu_2S\ (\text{or } Ag_2S) + 2\,H_2O$$

Hydrogen sulfide causes the precipitation of sulfides from many heavy-metal salts. The classical qualitative analysis scheme depends on precipitation of the sulfides of Hg, Pb, Bi, Cu, Cd, As, Sb, and Sn under acid conditions and the sulfides of Co, Ni, Mn, Zn, and Fe under ammoniacal conditions.

Hydrogen sulfide reacts with molten sulfur and depresses the viscosity of the latter, particularly at 130–180°C; infrared (ir) spectral studies show that polysulfanes, H_2S_x, form. The average chain length of these polysulfanes is shorter than the equilibrium chain length of molten sulfur alone at the same temperature; consequently, the viscosity of the molten sulfur is markedly reduced (118,119).

Hydrogen sulfide reacts with olefins under various conditions forming mercaptans and sulfides (142,143). With ethylene it can react to ultimately give diethyl sulfide (144). With unsymmetrical olefins, the direction of addition can be controlled by the choice of either a free-radical initiator, including ultraviolet light, or an acidic catalyst (144):

$$CH_2{=}CH_2 + H_2S \longrightarrow CH_3CH_2SH \xrightarrow{CH_2=CH_2} (C_2H_5)_2S$$

In the presence of sulfur, a disulfide can be produced (145):

$$2\,CH_2{=}CH_2 + H_2S \longrightarrow 2\,CH_3CH_2SH \xrightarrow{S} C_2H_5SSC_2H_5$$

When free-radical initiation is used, cocatalysts, eg, phosphites (146), and uv photoinitiators, such as acetophenone derivatives (147) can be used to increase the rate and conversion of the olefins to the desired mercaptans.

If olefins with electron-withdrawing substituents are involved, the addition can be conducted with a basic catalyst.

$$H_2S + CH_2{=}CHCOOR \xrightarrow{\text{base}} HSCH_2CH_2COOR$$

$$H_2S + 2\,CH_2{=}CHCOOR \xrightarrow{\text{base}} S(CH_2CH_2COOR)_2$$

Hydrogen sulfide reacts with alcohols under acid-catalyzed conditions, usually with solid acidic catalysts at elevated temperatures:

$$CH_3OH + H_2S \longrightarrow H_2O + CH_3SH \xrightarrow{CH_3OH} CH_3SCH_3 + H_2O$$

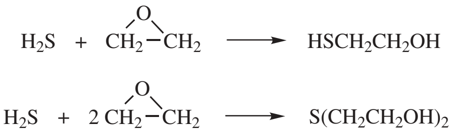
The catalyzed reaction of methanol and H_2S followed by reaction with sulfur yields dimethyl disulfide in good yield (148).

$$2\,CH_3OH + 2\,H_2S \xrightarrow{-2\,H_2O} 2\,CH_3SH \xrightarrow{S} CH_3SSCH_3 + H_2S$$

At 550–600°C, hydrogen sulfide reacts with chloroaromatic compounds forming thiophenols and diaryl sulfides (149):

$$H_2S + C_6H_5Cl \longrightarrow HCl + C_6H_5SH\,(\text{mainly}) + (C_6H_5)_2S$$

It also reacts with epoxides forming 2-hydroxyalkyl thiols, eg, 2-mercaptoethanol [60-24-2] and bis(2-hydroxyalkyl) sulfides, such as bis(2-hydroxyethyl) sulfide [111-48-8]; both products are made commercially:



Hydrogen sulfide reacts with nitriles in the presence of a basic catalyst forming thioamides. A commercial example is its addition to cyanamide with the formation of thiourea [62-56-6]:

$$H_2S + NH_2C\equiv N \longrightarrow NH_2\overset{\overset{\displaystyle S}{\|}}{C}NH_2$$

4.3. Manufacture. Small cylinders of hydrogen sulfide are readily available for laboratory purposes, but the gas can also be easily synthesized by action of dilute sulfuric or hydrochloric acid on iron sulfide, calcium sulfide [20548-54-3], zinc sulfide [1314-98-3], or sodium hydrosulfide [16721-80-5]. The reaction usually is run in a Kipp generator, which regulates the addition of the acid to maintain a steady hydrogen sulfide pressure. Small laboratory quantities of hydrogen sulfide can be easily formed by heating at 280–320°C a mixture of sulfur and a hydrogen-rich, nonvolatile aliphatic substance, eg, paraffin. Gas evolution proceeds more smoothly if asbestos or diatomaceous earth is also present.

Commercial-scale processes have been developed for the production of hydrogen sulfide from heavy fuel oils and sulfur, as well as from methane, water vapor, and sulfur. The latter process can be carried out in two steps: reaction of methane with sulfur to form carbon disulfide and hydrogen sulfide followed by hydrolysis of carbon disulfide (150).

Hydrogen sulfide has been produced in commercial quantities by the direct combination of the elements. The reaction of hydrogen and sulfur vapor proceeds at ~500°C in the presence of a catalyst, eg, bauxite, an aluminosilicate, or cobalt molybdate. This process, which was practiced for many years at the Hooker Chemical plant in Niagara Falls, N.Y., yields hydrogen sulfide that is of good purity and is suitable for preparation of sodium sulfide and sodium hydrosulfide. Most hydrogen sulfide used commercially is either a by-product or is obtained from sour natural gas.

4.4. Recovery from Gas Streams. The crude oil refined in the United States contains varying amounts of sulfur, eg, 0.04 wt% in Pennsylvania crude to ~5 wt% in heavy Mississippi crude. Hydrodesulfurization is becoming increasingly important as a refinery operation. More than 90% of the sulfur in crude oils is accounted for in the gas–oil and coke-distillate fractions. The sulfur compounds are mostly acyclic and cyclic sulfides; many of the latter are highly stable aromatic types, eg, benzothiophenes. Their removal is accomplished by passing the sulfur-rich fractions through a fixed-bed catalyst with hydrogen, which is generally by-product hydrogen from catalytic reforming. Besides conversion of 80–90% of the sulfur compounds to hydrogen sulfide, the hydrocarbon saturation is increased. The hydrogen sulfide is usually converted by Claus process oxidation to sulfur (see SULFUR REMOVAL AND RECOVERY).

4.5. Corrosivity. Anhydrous hydrogen sulfide has a low general corrosivity toward carbon steel, aluminum, Inconel, Stellite, and 300-series stainless steels at moderate temperatures. Temperatures greater than ~260°C can produce severe sulfidation of carbon steel. Alternative candidates for hydrogen sulfide service at higher temperatures and concentrations include 5 Cr–0.5 Mo and 9 Cr–1 Mo alloy steels, 400-series stainless steels, 300-series stainless steels, and Inconel. Stainless steels of low carbon content in the annealed condition are preferable.

Wet hydrogen sulfide can be quite corrosive to carbon steel; corrosion rates can exceed 2.5 mm/year. The actual corrosion rate depends on temperature and hydrogen sulfide concentration. All common metallic materials of construction, ie, carbon steels, Cr–Mo alloy steels, stainless steels, nickel-based alloys, and aluminum, can be used in wet hydrogen sulfide service depending on the process environment and the desired service life. In addition to general corrosion, wet hydrogen sulfide service can cause sulfide stress cracking. The atomic hydrogen created in the corrosion reaction diffuses into the metal that causes cracking. An important factor in reducing the likelihood of sulfide stress cracking is to limit the hardness of the base metal, weld metal, and base metal's heat-affected zone. An extensive compendium of hydrogen sulfide corrosion information has been published, and standards for sulfide-resistant metals for oil field use have been proposed (151,152). High nickel stainless steels and nickel-based alloys are the most resistant to sulfide attack under simulated deep oil- and gas-well environments (153). In the case of hydrogen sulfide copper or copper-bearing alloys are not to be used on any process equipment and associated instruments, controls, or electrical–mechanical equipment.

4.6. Economic Aspects. Most hydrogen sulfide is made and used captively or sold by pipeline at prices that are highly variable, depending on locality. Production in the United States exceeds 1.1×10^6 t/year. It has been estimated that 2.4×10^6 t/year of sulfur are recovered from H_2S-containing refinery streams and 1.8×10^6 t/year of sulfur are recovered from H_2S-containing natural gas (154).

Sulfuric acid production in 1995 was estimated to consume 110,000 metric tons of H_2S (155).

4.7. Analytical Methods.

A method recommended by NIOSH for measurement of hydrogen sulfide in air involves drawing a known volume of air through a desiccant tube containing sodium sulfate to remove water vapor. A tube containing a molecular sieve is then used to trap hydrogen sulfide, which is subsequently desorbed thermally and analyzed by gas chromatography. This method is useful for analysis to 15–60 mg/m^3 (156). An alternative method involves aspirating a measured volume of air through an alkaline suspension of cadmium hydroxide. Cadmium sulfide precipitates, and the collected sulfide is determined by spectrophotometric measurement of the methylene blue produced by reaction of the sulfide with an acid solution of *N,N*-dimethyl-*p*-phenylenediamine and ferric chloride. This method is useful to 8.5–63 mg/m^3 (157).

A simple laboratory method for detecting hydrogen sulfide is the use of lead acetate paper, which darkens upon formation of lead sulfide. Instruments containing a moving tape treated with lead acetate and having an optical device for measuring the reflectance of the tape have been devised for monitoring the presence of hydrogen sulfide. Detector tubes, eg, Draeger tubes, are available for fast, semiquantitative measurement of hydrogen sulfide in air. Electronic devices based on solid-state sensors (qv) have also become available for continuous monitoring of hydrogen sulfide (158).

Ultraviolet spectrophotometry is a widely used method for measuring hydrogen sulfide and sulfur dioxide in Claus process control (159). Special heated sample probes are available to avoid the problem of water condensation.

4.8. Health and Safety Factors.

Hydrogen sulfide has an extremely high acute toxicity and has caused many deaths both in the workplace and in areas of natural accumulation, eg, cisterns and sewers (160,161). Hydrogen sulfide can be hazardous to workers in the gas, oil chemical, geothermal energy, and viscose rayon industries and workers in sewer systems, tanneries, mining, drilling, smelting, animal-waste disposal, and on fishing boats (162–164).

Brief exposure to hydrogen sulfide at a concentration of 140 mg/m^3 causes conjunctivitis and keratitis (eye damage), and exposures at above ~ 280 mg/m^3 cause unconsciousness, respiratory paralysis, and death. There is no conclusive evidence of adverse health effects from repeated long-term exposure to hydrogen sulfide at low concentrations, although there is some evidence pointing to nervous system, cardiovascular, gastrointestinal, and ocular disorders. Symptoms of low level exposure can include headache, nausea, insomnia, fatigue, and inflammation of the eyes and mucous membranes. Irritation of the eyes and respiratory system has been reported at concentrations < 1 ppm.

Hydrogen sulfide is especially dangerous when it occurs in low lying areas or confined workspaces or when it exists in high concentrations under pressure. Because of corrosion and embrittlement, hydrogen sulfide lines and fittings are prone to develop leaks. Hydrogen sulfide is fast acting and the exposed person may become unconscious quickly, with no opportunity to escape the contaminated space. Moreover, hydrogen sulfide has a deceptively sweet smell at 30–100 ppm and deadens the sense of smell above this range; therefore, its odor is an unreliable indicator of dangerous concentrations. Self-contained breathing apparatus or a supplied-air respirator is necessary for workers entering areas known or suspected to contain toxic levels of hydrogen sulfide. A summary of the effects of hydrogen sulfide exposure on humans is given in Table 4.

Because many lethal accidents have occurred when using or generating hydrogen sulfide, it is imperative that before using it the Material Safety Data Sheet (MSDS) for this product be thoroughly read and understood (165) and training is recommended. It is advisable to read a hydrogen sulfide users manual from the supplier that should discuss physical properties, health hazards, material of construction, storage, shipping container, recommended unloading, emergencies, and special precautions with rail−tank car use. OSHA exposure limits for H_2S are 10 ppm (14 mg/m^3) OSHA/TWA; 10 ppm is the NIOSH recommended 10-min ceiling.

Protective measures involve prompt detection and adequate ventilation. Continuous monitoring is recommended to signal an evacuation alarm if the workplace concentration > 70 mg/m^3 (50 ppm) and a warning alert if it is present at 15−70 mg/m^3 (10−50 ppm). Alberta, which has a major sulfur industry, permits the long-term presence of 0.004 mg/m^3. Various states have passed emission standards for effluent air or gas from stationary sources. A good summary of these regulations as of 1979 is available (161). In addition to processes to control emissions by scrubbing hydrogen sulfide from gas streams (166–168), considerable progress has been made in controlling smaller hydrogen sulfide emissions from sewage systems and industrial waste systems by use of hydrogen peroxide as an oxidant.

The mechanisms of toxicological and environmental effects have been recently reviewed (169). Hydrogen sulfide is able to act on plants either as a nutrient or as a toxin (169,170).

4.9. Uses. Most of the hydrogen sulfide recovered as a by-product is converted to elemental sulfur by the Claus process, or to sulfuric acid where there is a market for the acid near the source of the hydrogen sulfide (see SULFURIC ACID AND SULFUR TRIOXIDE). Hydrogen sulfide is also used to prepare various inorganic sulfides, notably sodium sulfide and sodium hydrosulfide, which are used in the manufacture of dyes (qv), rubber chemicals (qv), pesticides, polymers, plastics additives, leather (qv), and pharmaceuticals (qv). A large amount of sodium hydrosulfide or sodium sulfide is used and largely recycled in kraft pulping; hydrogen sulfide can be used for replenishing the sulfide content (see PULP). An important industrial application is the reaction of hydrogen sulfide with alcohol or olefins (alkenes) to produce thiols (qv) or mercaptans. Hydrogen sulfide is also used for presulfiding petroleum hydrocracking catalysts.

In metallurgy, hydrogen sulfide is used to precipitate copper sulfide from nickel−copper-containing ore leach solutions in Alberta, Canada, or to precipitate nickel and cobalt sulfides from sulfuric acid leaching of laterite ores in Moa Bay, Cuba (154) (see EXTRACTIVE METALLURGY). Hydrogen sulfide is also used in the production of heavy water for the nuclear industry (104).

5. Sodium Hydrosulfide

Sodium hydrosulfide (sodium hydrogen sulfide) is usually made from hydrogen sulfide by reaction with one molar equivalent of sodium hydroxide. Many of the applications are discussed under hydrogen sulfide. The product is usually made from by-product hydrogen sulfide. Many U.S. producers have the by-product as 22–46% aqueous solution, which mostly goes to the pulp and paper industry. PPG Industries sells it as a high grade flaked product, 70–72% NaHS.

Annual U.S. production, reported on a 100% NaHS basis, and excluding low purity low concentration by-product, is in the 100,000 ton vicinity. List price for the flaked product is in the $0.33/lb range (2005).

Besides the pulp and paper usage, sodium hydrosulfide goes into the mineral flotation as a depressant for sulfide ore (mostly copper ore), manufacture of sulfur dyes, sulfide elastomers, dehairing of hides in leather tanning, precipitation of metals in waste water, and miscellaneous reducing agent applications. A growing use is probably for conversion to sodium sulfide for manufacture of polyphenylene sulfide, reported (August 2005) to be growing at 10%/year.

6. Sodium Sulfide

Sodium sulfide is usually made from hydrogen sulfide by reaction with two molar equivalents of sodium hydroxide. Sodium sulfide can also be made by reducing barite ore (barium sulfate) by coal or coke at $\sim 800^{\circ}C$ to produce crude barium sulfide, which is then reacted with sodium carbonate to make barium carbonate (a commercial product) and aqueous sodium sulfide. An old process for reducing sodium sulfate with powdered coal is no longer used in the United States but the related reduction of sodium sulfate by organic carbon in pulp to produce sodium sulfide is conducted in some kraft pulp mills.

Merchant sodium sulfide is usually sold as fused crystals, 30–34% Na_2S, or flaked solid, 60–62% Na_2S. Only two U.S. producers are reported for the high purity sodium sulfide, Chemical Products Corp. (Cartersville, Ga.) and PPG Industries Inc., Natrium, W.Va. U.S. production of merchant Na_2S is in the 30,000 ton/year vicinity, of which $\sim 60\%$ is used in dehairing hides before tanning; 25% in miscellaneous chemical manufacturing, such as polysulfide elastomers and polyphenylene sulfide thermoplastic; and the remainder in dye manufacturing, ore flotation, and other uses. The use in kraft wood pulping is not included, because this usually does not entail purchase of pure sodium sulfide. The list price for the flaked product is in the $0.32/lb range (2005).

7. Hydrogen Polysulfides

Individual hydrogen polysulfides (sulfanes) have been characterized from H_2S_2 [13465-07-1] up to at least H_2S_8 [12026-49-2] (171). These are of no commercial utility by themselves, although sodium and calcium polysulfides, which are made by addition of sulfur to the corresponding monosulfides, are used commercially. The atmospheric boiling point of H_2S_2 is $70.7^{\circ}C$ and the boiling point of H_2S_3 [13845-23-3] is $69^{\circ}C$ at 0.3 kPa (2 mmHg). The higher hydrogen polysulfides have been separated by fractional distillation at 13 mPa (10^{-4} mmHg). All are unstable. The reaction of Na_2S_n (from $Na_2S + S_8$) with SCl_2 in anhydrous and air-free C_1–C_5 alcohols is reported to yield sulfanes (H_2S_n where $n = 2$–16) and these were analyzed by hplc, using a C_{18}-bonded phase and methanol as the eluent (172). The sulfanes decompose slowly under argon yielding H_2S and

S_n homocycles. With alkali they decompose rapidly to H_2S and S_8. The high resolution ftir spectrum of H_2S_2 has been reported (173). Hydrogen polysulfides are extremely unstable even to traces of alkalies, and must be kept in HCl-treated glass or silica vessels because ordinary glass is too alkaline. A mixture of hydrogen polysulfides can be prepared by addition of an alkali polysulfide to acid (174).

The H_2S_x sulfanes are the subject of several reviews (171,175). Except for hydrogen sulfide these have no practical utility as isolated chemicals. However, they are key intermediates in sulfur recovery processes and serve to depress the viscosity of molten sulfur (176). They are not removable from elemental sulfur by mere physical degassing.

Sodium polysulfide (principally tetrasulfide) [12034-39-8] is available commercially as a 28–40 wt% aqueous solutions and is used to dehair hides in tanneries, as an ore flotation agent, in the preparation of sulfur dyes (qv), and for metal sulfide finishes (see LEATHER; MINERAL RECOVERY AND PROCESSING). It is a useful reactant for destroying toxic cyanide (eg, in refinery streams) and converting it to relatively harmless thiocyanate. In this application, it is more controllable and selective than the less-stable ammonium polysulfide that is used for the same purpose. Polysulfide salts also have been claimed to be useful corrosion inhibitors for oil field piping (177).

Another area of practical importance of the higher sulfanes relates to their formation in sour-gas wells from sulfur and hydrogen sulfide under pressure and their subsequent decomposition that causes well plugging (178). The formation of high sulfanes in the recovery of sulfur by the Claus process also may lead to persistance of traces of hydrogen sulfide in the sulfur thus produced (95). Quantitative determination of H_2S_x and H_2S in Claus process sulfur requires the use of a catalyst, eg, PbS, to accelerate the breakdown of H_2S_x (179).

8. Sulfur Halides

Sulfur forms several series of halides with all of the halogens except iodine. The fluorides include the commercially important sulfur hexafluoride [2551-62-4] (see FLUORINE COMPOUNDS, INORGANIC).

8.1. Sulfur Monochloride.

Physical Properties. Sulfur monochloride [10025-67-9], disulfur dichloride, S_2Cl_2, is a yellow-orange liquid with a characteristic pungent odor. It was first discovered as a chlorination product of sulfur in 1810. Table 5 provides a list of the physical properties.

Chemical Properties. The chemistry of the sulfur chlorides has been reviewed (185,186). Sulfur monochloride is stable at ambient temperature, but undergoes exchange with dissolved sulfur at 100°C, indicating reversible dissociation. When distilled at its atmospheric boiling point, it undergoes some decomposition to the dichloride, but decomposition is avoided with distillation at ~ 6.7 kPa (50 mmHg). At > 300°C, substantial dissociation to S_2 and Cl_2 occurs. Sulfur monochloride is noncombustible at ambient temperature, but at elevated temperatures it decomposes to chlorine and sulfur (181). The sulfur then is capable of burning to sulfur dioxide and a small proportion of sulfur trioxide.

Sulfur monochloride is hydrolyzed at a moderate rate by water at room temperature but rapidly, even violently, at higher temperatures or if heat is not conducted away. The products are hydrochloric acid, sulfur dioxide, sulfurous acid, hydrogen sulfide, and thiosulfurous acid. In the vapor state, the hydrolysis rate is slow and involves disproportionation of the primary sulfur-containing hydrolysis products, but corrosive hydrochloric acid is formed immediately:

$$S_2Cl_2 + 2\,H_2O \longrightarrow 2\,HCl + SO_2 + H_2S$$

In solution, the hydrogen sulfide and sulfur dioxide [7446-09-5] thus formed react to producing polythionic acids and elemental sulfur.

Various reducing agents, eg, hydrogen iodide, can abstract chlorine from sulfur monochloride leaving elemental sulfur:

$$S_2Cl_2 + 2\,HI \longrightarrow I_2 + 2\,HCl + 2\,S^0$$

This reaction is useful analytically.

Some metallic oxides and sulfides are chlorinated by sulfur chlorides:

$$ZnS + S_2Cl_2 \longrightarrow ZnCl_2 + 3\,S^0$$

Sulfur trioxide [7446-11-9] reacts with sulfur monochloride to produce pyrosulfuryl chloride [7791-27-7], $ClSO_2OSO_2Cl$.

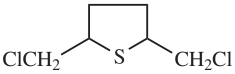
Hydrogen sulfide can react with S_2Cl_2 to produce, depending on conditions, a mixture of sulfanes (H_2S_x where $x > 1$) or dichlorosulfanes (S_xCl_2, where $x > 2$). These compounds tend to be unstable at ambient temperatures.

Numerous organic reactions of sulfur monochloride are of practical and commercial importance. Of particular importance is the reaction of sulfur monochloride with olefins to yield various types of addition products (186). With ethylene, the severe vesicant bis(2-chloroethyl) sulfide [505-60-2] (mustard gas) forms with elemental sulfur and polysulfides (see CHEMICALS IN WAR). Propylene reacts similarly:

$$2\,CH_2{=}CH_2 + S_2Cl_2 \longrightarrow (ClCH_2CH_2)_2S + S$$

Higher olefins appear to yield mainly bis(2-chloralkyl) disulfides.

The reaction of S_2Cl_2 with 1,5-hexadiene gives cyclic sulfide containing chlorines I and II which at 20°C give upon isomerization the stable mixture of 35% (**5**) and 65% (**6**) 187.



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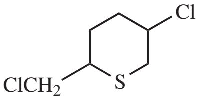


(6)

Sulfurized olefins (S_2Cl_2 plus isobutene) are further reacted with S and Na_2S to give products useful as extreme pressure lubricant additives (188,189). The reaction of unsaturated natural oils with sulfur monochloride gives resinous products known as factice, which are useful as art-gum erasers and rubber additives (190,191). The addition reaction of sulfur monochloride with unsaturated polymers, eg, natural rubber, produces cross-links and thus serves as a means for vulcanizing rubber at moderate temperatures. The photochemical cross-linking of polyethylene has also been reported (192).

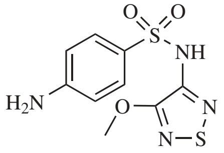
Using sulfur trioxide plus chlorine, or sulfur dioxide plus chlorine, sulfur monochloride yields thionyl chloride [7719-09-7], $SOCl_2$. Various nucleophilic reactions can displace the chlorine atoms of sulfur monochloride:

$$S_2Cl_2 + 2\,RONa \longrightarrow ROSSOR + 2\,NaCl$$

$$S_2Cl_2 + 2\,RSH \longrightarrow RS_4R + 2\,HCl$$

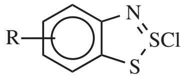
$$S_2Cl_2 + 4\,R_2NH \longrightarrow R_2NSSNR_2 + 2\,R_2NH\cdot HCl$$

The reaction with morpholine is used to make a commercial vulcanizing agent dithiodimorpholine. Reaction with *p*-chlorophenol gives the microbiocide Fenticlor, 2,2'-thiobis(4-chlorophenol). Also, it can be used to make a thiadiazole-containing sulfa drug, Sulfametrol



It can also be used in the synthesis of the pesticides fipronil and carbosulfan as the source of a sulfur atom.

Reaction with anilines yields the Herz compounds, which are intermediates for certain sulfur dyes (qv) as well as vulcanizing agents for rubber (193).



Manufacture. Sulfur monochloride is made commercially by direct chlorination of sulfur, usually in a heel of sulfur chloride from a previous batch. The chlorination appears to proceed stepwise through higher sulfur chlorides (S_xCl_2, where $x > 2$). If conducted too quickly, the chlorination may yield products containing SCl_2 and S_xCl_2 as well as S_2Cl_2. A catalyst, eg, iron, iodine, or a trace of ferric chloride, facilitates the reaction. The manufacture in the absence of Fe and Fe salts at 32–100°C has also been reported (193–195).

The commercial manufacture of carbon tetrachloride by chlorination of carbon disulfide yields sulfur monochloride.

$$CS_2 + 3\,Cl_2 \longrightarrow CCl_4 + S_2Cl_2$$

The sulfur monochloride formed in this reaction can be treated with additional carbon disulfide in the presence of a catalyst to yield carbon tetrachloride and sulfur. Alternatively, the sulfur monochloride and carbon tetrachloride can be

$$CS_2 + 2\,S_2Cl_2 \longrightarrow CCl_4 + 6\,S^0$$

separated by careful distillation (qv) in an inert gas stream (196). Modern processes utilize continuous introduction of chlorine into liquid sulfur at ~240°C and 101 kPa (1 atm) (197). The commercial product is assayed for purity by gc (traditionally, by specific gravity determination). A typical commercial specification is 99.2 wt% sulfur monochloride minimum.

Shipment and Storage. Sulfur monochloride is minimally corrosive to carbon steel and iron when dry. If it is necessary to avoid discoloration caused by iron sulfide formation or chloride stress cracking, 310 stainless steel should be used. Sulfur monochloride is shipped in tank cars, tank trucks, and steel drums. When wet, it behaves like hydrochloric acid and attacks steel, cast iron, aluminum, stainless steels, copper and copper alloys, and many nickel-based materials. Alloys of 62 Ni–28 Mo and 54 Ni–15 Cr–16 Mo are useful under these conditions. Under DOT HM-181 sulfur monochloride is classified as a Poison Inhalation Hazard (PIH) Zone B, as well as a Corrosive Material (DOT Hazard Class B). Shipment information is available (184).

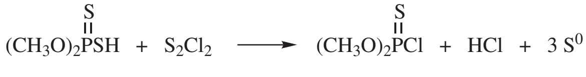
Uses. The reaction of S_2Cl_2 with aromatic compounds can yield disulfides or mixtures of mono-, di-, and polysulfides.

$$S_2Cl_2 + 2\,C_6H_6 \longrightarrow (C_6H_5)_2S_x$$

A similar reaction with phenols is employed to make commercial vulcanizing agents and antioxidants (see ANTIOXIDANTS; ANTIOZONANTS).

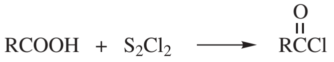
Sulfur monochloride also reacts with substituted phenols to give condensation products useful for rubber compounding (qv) (194). Arkema (formerly Elf Atochem) manufactures products known as Vultacs by the reaction of amylphenols and sulfur monochloride (153). A new family of oligomeric phenolic poly-(mainly tetra-)sulfides, made by reaction of sulfur monochloride plus extra sulfur with xylenol, is in development by Akzo Nobel for wood preservation (198,199).

Sulfur monochloride can act as a chlorinating agent in some reactions. For example, *O,O*-dialkyl phosphorodithioic acids [756-80-9] are converted to *O,O*-dialkyl phosphorochloridothioate:

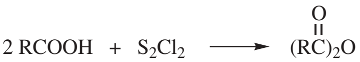


$$(CH_3O)_2\overset{\overset{S}{\|}}{P}SH + S_2Cl_2 \longrightarrow (CH_3O)_2\overset{\overset{S}{\|}}{P}Cl + HCl + 3\,S^0$$

Carboxylic acids can be converted to acid chlorides or anhydrides:



$$RCOOH + S_2Cl_2 \longrightarrow R\overset{\overset{O}{\|}}{C}Cl$$



$$2\,RCOOH + S_2Cl_2 \longrightarrow (R\overset{\overset{O}{\|}}{C})_2O$$

The principal commercial uses of sulfur monochloride are in the manufacture of lubricant additives and vulcanizing agents for rubber (191,200,201) (see LUBRICATION AND LUBRICANTS; RUBBER CHEMICALS). The preparation of additives for wear and load-bearing improvement of lubricating oils is generally carried out in two steps and the technology is described in numerous patents (155) (see SULFURIZATION AND SULFCHLORINATION). Also, some pharmaceuticals (Sulfametrol, Fenticlor) and agrochemicals (Fipronil, Carbosulfan) are reportedly manufactured using sulfur monochloride.

Economic Aspects. The price of sulfur monochloride in 2005 was ~ $0.90/kg bulk.

Health and Safety Factors. Sulfur monochloride is highly toxic and irritating by inhalation, and is corrosive to skin and eyes (202). A detailed toxicology update is available online (203). The American Conference of Governmental Industrial Hygienists (ACGIH) has set a TLV ceiling level of 1 ppm (5.5 mg/m^3) due to its irritation potential (204). Additionally, NIOSH has assigned an immediately dangerous to life or health (IDLH) concentration of 5 ppm (205). The OSHA permissible exposure limit is 1 ppm (6 mg/m^3). Pulmonary edema may result from inhalation. Because its vapor cannot be tolerated even at low concentrations, its presence serves as a warning factor. The irritation threshold of sodium monochloride is listed as 12 mg/m^3 (206). Sulfur monochloride is not highly flammable, having flash points of 118°C (closed-cup) and 130°C (open-cup) and an autoignition temperature of 234°C. Since sulfur chlorides react exothermically on contact with water forming highly toxic and corrosive fumes, dry chemicals, or carbon dioxide are recommended in fire fighting situations.

Sulfur monochloride, besides its benign uses, is a precursor for a chemical weapon (mustard gas) so that its commercial sale and export are regulated under the international chemical weapons treaty. Also, under the Superfund act (CERCLA), any sulfur monochloride release of 1000 lbs or more must be reported to the National Response Center.

8.2. Sulfur Dichloride. *Physical Properties.* Sulfur dichloride [10545-99-1], SCl_2, is a reddish or yellow fuming liquid that decomposes in moist air with the evolution of hydrogen chloride (207). Pure sulfur dichloride is unstable and is supplied commercially as a 72–82 wt% SCl_2 mixture, with sulfur monochloride comprising the remaining percentage. The melting point is reported in the range −121.5 to −61°C, and the boiling point with decomposition is 59°C. The sp. gr. is 1.621 at 15°C. Distillation of sulfur dichloride with minimal decomposition and improved storability requires the addition of a stabilizer, eg, PCl_3 (~ 0.1%).

The solubility of sulfur dichloride in water is not meaningful because it reacts rapidly. It is slightly soluble in aliphatic hydrocarbons and very soluble in benzene and carbon tetrachloride. The heat of formation is −22 kJ/mol (−5.3 kcal/mol) for the gas at 25°C (182).

Chemical Properties. Sulfur dichloride in the liquid state at ambient temperature is in equilibrium with sulfur monochloride and dissolved chlorine:

$$2\,SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2$$

The equilibrium constant is 0.013 at 18°C. Sulfur dichloride reacts violently with water, forming hydrogen chloride, sulfur dioxide, hydrogen sulfide, sulfur, and a mixture of thionic acids.

Sulfur dichloride is oxidized by sulfur trioxide or chlorosulfuric acid [7790-94-5] (qv) to form thionyl chloride:

$$SCl_2 + SO_3 \longrightarrow SOCl_2 + SO_2$$

$$SCl_2 + ClSO_3H \longrightarrow SOCl_2 + SO_2 + HCl$$

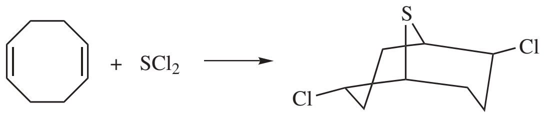
Economic Aspects. The price of sulfur dichloride was $0.80/kg bulk in 2005. Akzo Nobel is the only U.S. producer with merchant sales. Some companies still produce sulfur dichloride for captive use (208); Occidental Chemical Company ended sulfur dichloride production in late 1993.

Chemical Reactions. Sulfur dichloride reacts with an excess of sulfur trioxide forming pyrosulfuryl chloride:

$$SCl_2 + 3\,SO_3 \longrightarrow S_2O_5Cl_2 + 2\,SO_2$$

Sulfur dichloride undergoes many of the same reactions with organic compounds as described for sulfur monochloride. Addition to olefins affords a route to bis(2-chloroalkyl) sulfides and, in certain cases, heterocyclic sulfides (209,210).

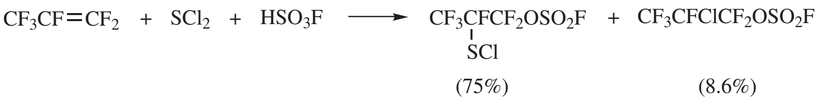
$$RCH{=}CH_2 + SCl_2 \longrightarrow (RCHClCH_2)_2S$$



With a few olefins, the addition can yield sulfenyl chlorides, eg, 2-dichloroethane sulfenyl chloride [2441-27-2]:

$$CHCl{=}CHCl + SCl_2 \longrightarrow Cl_2CHCHClSCl$$

Sulfur dichloride reacts with hexafluoropropene in the presence of fluorosulfonic acid at 30–60°C to give the following (211):

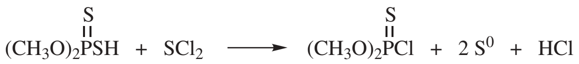


$$\underset{}{CF_3CF{=}CF_2 + SCl_2 + HSO_3F \longrightarrow \underset{\displaystyle (75\%)}{CF_3\underset{\displaystyle SCl}{\underset{|}{C}}FCF_2OSO_2F}} + \underset{\displaystyle (8.6\%)}{CF_3CFClCF_2OSO_2F}$$

Manufacture. The manufacture of sulfur dichloride is similar to that of sulfur monochloride, except that the last stage of chlorination proceeds slowly and must be conducted at temperatures < 40°C. The preparation of a high assay sulfur dichloride requires special techniques, eg, continuous chlorination during distillation or distillation with traces of phosphorus trichloride or phosphorus pentasulfide [1314-80-3] (212–214). Crude product containing 80 wt% sulfur dichloride to which is added 0.1 wt% phosphorus trichloride can be distilled to yield a 98–99 wt% pure sulfur dichloride, which can be stored for weeks at room temperature without appreciable change.

Shipment and Storage. Sulfur dichloride, if kept dry, is noncorrosive at ambient temperatures, thus carbon steel and iron can be used in the construction of tanks, piping, and drums. However, when water or humidity is present, materials resistant to hydrochloric acid must be used, eg, glass-lined pipe, Teflon, titanium, Hastelloy C, or possibly a chemically resistant, glass-reinforced polyester. Threaded pipe joints should be assembled with Teflon tape. Hoses should be constructed with a Teflon inner lining with the outer tube constructed of Neoprene or braided 316 stainless steel protected by an adequate thickness of Teflon. Sulfur dichloride should be stored away from heat and away from direct rays of the sum. Toluene and sulfur dichloride react exothermically when catalyzed by iron or ferric chloride. Safety precautions should be followed when such a mixture is present (215).

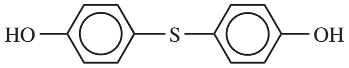
Uses. Sulfur dichloride was used as a chlorinating agent to convert a P(S)SH group to a P(S)Cl in the manufacture of parathion [56-38-2], one of the early phosphate insecticides, now largely replaced by less-toxic alternatives (see INSECT CONTROL TECHNOLOGY):



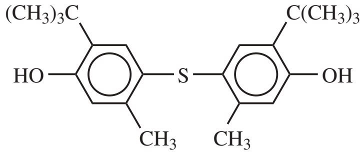
$$(CH_3O)_2\overset{\overset{S}{\|}}{P}SH + SCl_2 \longrightarrow (CH_3O)_2\overset{\overset{S}{\|}}{P}Cl + 2\,S^0 + HCl$$

It is also useful in the rapid vulcanization of rubber, eg, in the preparation of thin rubber goods by coating molds or fabrics with rubber latex. Cross-linked gums, factice, useful as rubber diluents and processing aids, may be made from unsaturated oils and sulfur dichloride (as well as with sulfur monochloride). The cross-linking ability of sulfur dichloride has been utilized to modify drying oils for varnishes and inks.

An insecticide intermediate, 4,4′-thiobisphenol [2664-63-3] is made from sulfur dichloride and phenol:



Antioxidants used in lubricants are also made by reaction of sulfur dichloride with phenols:



The addition of sulfur dichloride to 1,2-dichloroethylene yields 1,2,2-trichloroethanesulfenyl chloride which, after further chlorination to 1,1,2,2-tetrachloroethanesulfenyl chloride [1185-09-7], is used to produce the fungicide captafol [2425-06-1]. Lubricating oil additives of types similar to those produced using sulfur monochloride are a significant application for sulfur dichloride (216). The chemistry of sulfur dichloride in the synthesis of sulfur-containing heteroatomic rings has been reviewed (217).

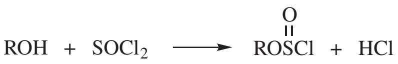
9. Oxyhalides

9.1. Thionyl Chloride [7719-09-7]. Thionyl chloride is a colorless liquid with a choking odor. Selected physical and thermodynamic properties are listed in Table 6. Thionyl chloride is miscible with many organic solvents including chlorinated hydrocarbons and aromatic hydrocarbons. It reacts quickly with water to form HCl and SO_2. Thionyl chloride is stable at room temperature; however, slight decomposition occurs just slightly above its boiling point, so prolonged refluxing should be avoided. It decomposes fairly rapidly $>150°C$ and completely decomposes at $500°C$ to chlorine, sulfur dioxide, and sulfur monochloride. Thionyl chloride is nonflammable.

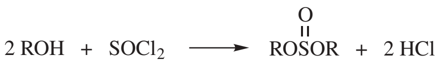
Chemical Properties. Thionyl chloride chemistry has been reviewed (219–223). Significant inorganic reactions of thionyl chloride include its reactions with sulfur trioxide to form pyrosulfuryl chloride and with hydrogen bromide to form thionyl bromide [507-16-4]. With many metal oxides it forms the corresponding metal chloride plus sulfur dioxide, and therefore affords a convenient means for preparing anhydrous metal chlorides.

The reactions of thionyl chloride with organic compounds having hydroxyl groups are important. Alkyl chlorides, alkyl sulfites, or alkyl chlorosulfites form from its reaction with aliphatic alcohols, depending on reaction conditions, stoichiometry, and the alcohol structure:

$$\mathrm{ROH} + \mathrm{SOCl_2} \longrightarrow \mathrm{RCl} + \mathrm{SO_2} + \mathrm{HCl}$$



$$\mathrm{ROH} + \mathrm{SOCl_2} \longrightarrow \mathrm{RO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{Cl} + \mathrm{HCl}$$



$$2\,\mathrm{ROH} + \mathrm{SOCl_2} \longrightarrow \mathrm{RO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{OR} + 2\,\mathrm{HCl}$$

These reactions can be catalyzed by bases, eg, pyridine, or by Lewis acids, eg, zinc chloride. In the case of asymmetric alcohols, steric control, ie, inversion, racemization, or retention of configuration at the reaction site, can be achieved by the choice of reaction conditions (223,224). Some alcohols dehydrate to olefins when treated with thionyl chloride and pyridine. Conditions for converting tertiary alcohols to tertiary alkyl chlorides have been patented (225).

With phenols, thionyl chloride forms the aryl chlorides only in exceptional cases, eg, with trinitrophenol (picric acid). The reaction of thionyl chloride with primary amines produces thionylamines.

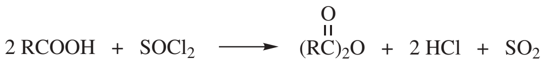
$$\mathrm{RNH_2} + \mathrm{SOCl_2} \longrightarrow \mathrm{RN{=}S{=}O} + 2\,\mathrm{HCl}$$

Sulfamic acids yield sulfamyl chlorides, which are useful intermediates for several herbicide syntheses.

$$\mathrm{RNHSO_3H} + \mathrm{SOCl_2} \longrightarrow \mathrm{RNHSO_2Cl} + \mathrm{HCl} + \mathrm{SO_2}$$

The reaction of thionyl chloride with carboxylic acids yields either acid chlorides or, in some cases, anhydrides depending on the stoichiometry:

$$\mathrm{RCOOH + SOCl_2 \longrightarrow R\overset{\overset{O}{\|}}{C}Cl + HCl + SO_2}$$



$$\mathrm{2\,RCOOH + SOCl_2 \longrightarrow (R\overset{\overset{O}{\|}}{C})_2O + 2\,HCl + SO_2}$$

This route to acid chlorides is often preferred over the alternative use of phosphorus trichloride because the by-products, SO_2 and HCl, are gaseous and easily removed. On the other hand, the use of phosphorus trichloride yields phosphorous acid as a by-product. This can decompose exothermically with evolution of toxic and flammable phosphine if overheated, however, phosphorous acid is saleable as a valuable by-product on a commercial scale.

The conversion of carboxylic acids to acid chlorides using thionyl chloride is often facilitated by the presence of a *N,N*-disubstituted amide.

Manufacture. Thionyl chloride may be made by any of the following reactions:

$$\mathrm{SCl_2 + SO_3 \longrightarrow SOCl_2 + SO_2}$$

$$\mathrm{SCl_2 + SO_2 + Cl_2 \longrightarrow 2\,SOCl_2}$$

$$\mathrm{SCl_2 + SO_2Cl_2 \longrightarrow 2\,SOCl_2}$$

The sulfur dichloride can be fed as such or produced directly in the reactor by reaction of chlorine with sulfur monochloride. In a batch process (226), a glass-lined jacketed iron vessel is charged with either sulfur monochloride or sulfur dichloride and ~1% of antimony trichloride as a catalyst. Chlorine is introduced into the reactor near the bottom. Liquid oleum is added to the reactor at such a rate that the temperature of the reaction mass is held at ~25°C by the use of cooling water in the jacket.

When the batch is completed, a slight excess of oleum and chlorine is added to reduce to a minimum the residual SCl_2. Because thionyl chloride combines readily with sulfur trioxide to form the relatively stable pyrosulfuryl chloride, it is necessary to maintain the concentration of sulfur trioxide in the reaction mass at a low level; hence, the addition of oleum to sulfur chloride rather than the reverse. When all of the reactants are added, heat is applied to the jacket of the reactor and the batch is refluxed until most of the sulfur dioxide, hydrogen chloride, and chlorine are eliminated. The thionyl chloride is then distilled from the reactor.

In another process, sulfur monochloride, sulfur dioxide, and chlorine are allowed to react at 200°C in the presence of an activated carbon catalyst (227):

$$\mathrm{S_2Cl_2 + 2\,SO_2 + 3\,Cl_2 \longrightarrow 4\,SOCl_2}$$

Using a 0–10% excess of chlorine and 100% excess of sulfur dioxide, conversions of ~50% are obtained. The liquids in the reaction product are condensed and separated, the sulfur mono- and dichloride are returned for further reaction, and the excess gases are also recycled, producing an ultimate yield near 100% on all reactants.

At present, thionyl chloride is probably produced commercially by the continuous reaction of sulfur dioxide (or sulfur trioxide) with sulfur monochloride (or sulfur dichloride) mixed with excess chlorine. The reaction is conducted in the gaseous phase at elevated temperature over activated carbon (228). Unreacted sulfur dioxide is mixed with the stoichiometric amount of chlorine and allowed to react at low temperature over activated carbon to form sulfuryl chloride, which is fed back to the main thionyl chloride reactor. A process for the comanufacture of thionyl chloride and phosphorus oxychloride from chlorine, sulfur dioxide, and phosphorus trichloride has been patented (229). A number of processes have been devised for purifying thionyl chloride. A recommended laboratory method involves distillation from quinoline and boiled linseed oil. Commercial processes involve adding various high boiling olefins such as styrene (qv) to react with the sulfur chlorides to form adducts that remain in the distillation residue when the thionyl chloride is redistilled (230). Alternatively, sulfur can be fed into the top of the distillation column to react with the sulfur dichloride (231). Commercial thionyl chloride has a purity of 98–99.6% minimum, having sulfur dioxide, sulfur chlorides, and sulfuryl chloride as possible impurities. These can be determined by gc (232).

Storage and Shipping. Thionyl chloride is classified as a corrosive material; it is shipped and stored in glass-lined steel tanks, zinc-coated (galvanized) steel drums, or special plastic drums having a DOT permit. Stainless steel (304L or 316L) may be used if all traces of moisture are excluded. Thionyl chloride stored in tanks or drums should be kept cool and away from direct sunlight and water.

Economic Aspects. The price of thionyl chloride in mid-1995 was $1.21/kg. As of late 1996 there was only one U.S. producer, Bayer (Baytown, Texas). Oxychem discontinued production in 1992. The remaining U.S. producer, Bayer (Baytown, Texas) closed their plant in 1997. In 2005, Lanxess (former Bayer) is the leading producer with a plant in Leverkusen, Germany.

Health and Safety Factors. Thionyl chloride is a reactive acid chloride that can cause severe burns to the skin and eyes and acute respiratory tract injury upon vapor inhalation. The hydrolysis products, ie, hydrogen chloride and sulfur dioxide, are believed to be the primary irritants. Depending on the extent of inhalation exposure, symptoms can range from coughing to pulmonary edema (233). The LC_{50} (rat, inhalation) is 500 ppm (1 h), the DOT label is Corrosive, Poison, and the OSHA PEL is 1 ppm (234). The safety aspects of lithium batteries (qv) containing thionyl chloride have been reviewed (235,236).

Although by itself nonflammable, thionyl chloride reacts violently with water so that fire fighters should use dry means of extinguishment of burning materials in the presence of large amounts of thionyl chloride.

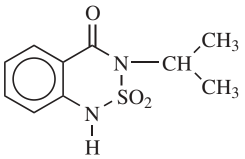
Thionyl chloride, besides its benign uses, is a precursor for a chemical weapon (mustard gas) so that its commercial sale and export are regulated under the international chemical weapons treaty. Also, under the Superfund act (CERCLA), any thionyl chloride release of 1000 lb (453.6 kg) or more must be reported to the National Response Center.

Uses. A principal use of thionyl chloride is in the conversion of acids to acid chlorides, which are employed in many syntheses of herbicides (qv), surfactants (qv), drugs, vitamins (qv), and dyestuffs. Possible larger-scale applications are in the preparation of engineering thermoplastics of the polyarylate type made from iso- and terephthaloyl chlorides, which can be made from the corresponding acids plus thionyl chloride (237) (see Engineering plastics).

The reactive intermediate, $(C_2H_5)_2NCH_2CH_2Cl{\cdot}HCl$, which is used to produce cationic starch, is made by the reaction of $(C_2H_5)_2NCH_2CH_2OH$ with thionyl chloride. A synthetic sweetener (qv), sucralose [56038-13-2], may be made by the reaction of sucrose or an acetate thereof with thionyl chloride to replace three hydroxy groups by chlorines (238–240).

An intermediate for the herbicide bentazone [25057-89-0] (**9**) can be prepared by the following reactions (224):

$$(CH_3)_2CHNH_2 + SO_3 \longrightarrow (CH_3)_2CHNHSO_3H + SOCl_2 \longrightarrow (CH_3)_2CHNHSO_2Cl$$



(**9**)

An example of a sulfite ester made from thionyl chloride is the commercial insecticide endosulfan [115-29-7]. A stepwise reaction of thionyl chloride with two different alcohols yields the commercial sulfite ester miticide, propargite [2312-35-8] (241). Thionyl chloride also has applications as a coreactant (presumably taking up water) in sulfonations and chlorosulfonations. A patent describes the use of thionyl chloride in the preparation of a key intermediate, bis(4-chlorophenyl) sulfone [80-07-9], which is used to make a commercial polysulfone engineering thermoplastic (see Polymers containing sulfur, polysulfone) (242). The sulfone group is derived from chlorosulfonic acid; the thionyl chloride may be considered a coreactant that removes water (see Sulfolanes and sulfones).

High energy density batteries with long shelf life, developed originally for military use, are based on lithium and thionyl chloride. These batteries are used in backup or standby power sources for computer, missile, sensors, and telephone systems (243–247).

9.2. Sulfuryl Chloride. *Physical Properties.* Sulfuryl chloride [7791-25-5], SO_2Cl_2, is a colorless to light yellow liquid with a pungent odor. Physical and thermodynamic properties are listed in Table 7. Sulfuryl chloride dissolves sulfur dioxide, bromine, iodine, and ferric chloride. Various quaternary alkylammonium salts dissolve in sulfuryl chloride to produce highly conductive solutions. Sulfuryl chloride is miscible with acetic acid and ether but not with hexane (248,249).

Chemical Properties. The chemistry of sulfuryl chloride has been reviewed (220,222,250). It is stable at room temperature, but readily dissociates to sulfur dioxide and chlorine when heated. The equilibrium constant has the following values (249):

$T(^\circ\mathrm{C})$:	30	40	50	102	159	191
$K\left(=\dfrac{[p\mathrm{SO_2}][p\mathrm{Cl_2}]}{[p\mathrm{SO_2Cl_2}]}\right)$:	2.92	5.13	8.34	240	902	1330

where $p =$ pressure in kPa (to convert to atm, divide by 101.3).

The decomposition of sulfuryl chloride is accelerated by light and catalyzed by aluminum chloride and charcoal. Many of the reactions of sulfuryl chloride are explainable on the basis of its dissociation products. Sulfuryl chloride reacts with sulfur at 200°C or at ambient temperature in the presence of aluminum chloride producing sulfur monochloride. It liberates bromine or iodine from bromides or iodides. Sulfuryl chloride does not mix readily with water and hydrolyzes rather slowly.

$$SO_2Cl_2 + 2\,H_2O \longrightarrow H_2SO_4 + 2\,HCl$$

The reaction of sulfuryl chloride with a stoichiometric amount of sulfuric acid produces chlorosulfuric acid [7790-94-5] (chlorosulfonic acid):

$$SO_2Cl_2 + H_2SO_4 \longrightarrow ClSO_3H$$

This latter reaction is reversible. Sulfuryl chloride can be fractionally distilled from boiling chlorosulfonic acid in the presence of a catalyst, eg, a mercuric salt.

Iodine reacts with sulfuryl chloride in the presence of aluminum chloride as catalyst-forming iodine chlorides. Sulfuryl chloride reacts with anhydrous ammonia yielding a series of sulfamides of the general formula $NH_2SO_2(NHSO_2)_nNH_2$, where n is 1 or higher. A cyclic compound of the formula $(SO_2NH)_3$ [13954-94-4] is also produced.

The organic chemistry of sulfuryl chloride involves its use in chlorination and sulfonation (222,251,252). As a chlorinating agent, sulfuryl chloride is often more selective than elemental chlorine. The use of sulfuryl chloride as a chlorinating agent often allows more convenient handling and measurement as well as better temperature control because of the lower heat of reaction as compared with chlorine. Sulfuryl chloride sometimes affords better selectivity than chlorine in chlorination of active methylene compounds (253–255):

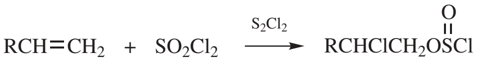
$$SO_2Cl_2 + CH_3COCH_2COOC_2H_5 \longrightarrow CH_3COCHClCOOC_2H_5 + HCl + SO_2$$

Alkanes can be simultaneously chlorinated and chlorosulfonated. This commercially useful reaction has been applied to polyethylene (256–258). Aromatics can be chlorinated on the ring. In the presence of a free-radical initiator, alkylaromatic compounds can be chlorinated selectively in the side chain. Methane can be chlorosulfonated to methanesulfonyl chloride at low temperature in the presence of a free-radical initiator, such as urea plus hydrogen peroxide, and in the presence of a promoter, such as rhodium chloride, using sulfuric acid as solvent (259). Ring chlorination can be selective. A patent shows chlorination of 2,5-dichloro- to 2,4,5-trichlorophenoxyacetic acid free of the toxic tetrachlorodibenzodioxins (260). The selectivity to the p-isomer in chlorination of toluene can be catalyzed by zeolite, and sulfuryl chloride is somewhat more selective than chlorine

(261). With alkenes, depending on conditions, the chlorination can be additive or substitutive. The addition of sulfuryl chloride can occur to form a 2-chloroalkanesulfonyl chloride (262).

$$\mathrm{RCH{=}CH_2 + SO_2Cl_2 \longrightarrow RCHClCH_2SO_2Cl}$$

However, when sulfur monochloride is used as the catalyst, chlorosulfites form.



$$\mathrm{RCH{=}CH_2 + SO_2Cl_2 \xrightarrow{S_2Cl_2} RCHClCH_2O\overset{\overset{O}{\|}}{S}Cl}$$

Sulfuryl chloride can be reacted with some alcohols to produce mixtures of sulfate esters, said to be useful as dyeing auxiliaries (263). With alkylamines, sulfuryl chloride can produce alkylsulfamoyl chlorides, which are useful intermediates in herbicide syntheses.

$$\mathrm{RNH_2{\cdot}HCl + SO_2Cl_2 \longrightarrow RNHSO_2Cl + 2\,HCl}$$

Manufacture. The preparation of sulfuryl chloride is carried out by feeding dry sulfur dioxide and chlorine into a water-cooled glass-lined steel vessel containing a catalyst, eg, activated charcoal. Alternatively, chlorine is passed into liquefied sulfur dioxide at ~0°C in the presence of a dissolved catalyst, eg, camphor, a terpene hydrocarbon, an ether, or an ester. The sulfuryl chloride is purified by distillation; the commercial product is typically 99 wt% pure, as measured by ASTM distillation method D850.

Shipment and Storage. To harmonize the DOT regulations with the UN regulations, sulfuryl chloride must be shipped in pressure-rated vessels. A double-wall disposable drum is required for drum shipments. With caution, dilute alkali can be used to hydrolyze and dispose of residual sulfuryl chloride. Dry steel tanks can be used to store sulfuryl chloride, but some corrosion may occur; lead, nickel, glass, Teflon, 310 stainless steel, or baked phenolics (tested for this service) are preferred. It is important to prevent exposure to atmospheric moisture and vent any hydrogen chloride pressure that builds up. Sulfuryl chloride should also be protected from prolonged exposure to strong light.

Economic Aspects. The truckload price of sulfuryl chloride in 2005 was ~$2.50/kg. Occidental Chemical Company (Niagara Falls, N.Y.) was the last U.S. merchant producer. Lanxess (former Bayer) produces it in Leverkusen, Germany. It may be made and used captively by DuPont for manufacture of their chlorosulfonated Hypalon elastomer.

Health and Safety Factors. Sulfuryl chloride is both corrosive to the skin and toxic upon inhalation. The TLV suggested by the manufacturer is 1 ppm. The vapors irritate the eyes and upper respiratory tract, causing prompt symptoms ranging from coughing to extreme bronchial irritation and pulmonary edema. The DOT label is Corrosive, Poison.

Uses. Uses of sulfuryl chloride include the manufacture of chlorophenols, eg, chlorothymol for use as disinfectants. It is also used in the manufacture of α-chlorinated acetoacetic derivatives, eg, $CH_3COCHClCOOC_2H_5$, which are precursors for important substituted imidazole drugs, phosphate insecticides, and fungicides (253,254). Other herbicide synthesis uses of sulfuryl chloride in which compounds with SO_2N linkages are produced have been reported. Sulfuryl chloride is believed to be used captively by DuPont in the manufacture of chlorosulfonated polyethylene [9008-08-6]. Process improvements have been the subject of DuPont and Toyo Soda patents (256–258).

Lithium sulfuryl chloride batteries have been developed for uses similar to the lithium thionyl chloride batteries (qv), but they have higher energy density due to higher voltage, and higher current capability due to higher conductivity.

10. Sulfur Nitrides

The sulfur nitrides have been the subject of several reviews (264–266). Although no commercial applications have as yet been developed for these compounds, some interest was stimulated by the discovery that polythiazyl, a polymeric sulfur nitride $(SN)_x$, with metallic luster, is electroconductive in the metallic range (see INORGANIC HIGH POLYMERS) (266–268). Other sulfur nitrides are unstable. Tetrasulfur nitride is explosive and shock sensitive.

11. Sulfur Oxides

Numerous oxides of sulfur have been reported and those that have been characterized are SO [13827-32-2], S_2O [20901-21-7], S_nO ($n = 6-10$), SO_2, SO_3, and SO_4 [12772-98-4]. Among these, SO_2 and SO_3 are of principal importance. Sulfur oxide chemistry has been reviewed (269–271). Sulfur trioxide, SO_3, is discussed elsewhere in this *Encyclopedia* (see SULFURIC ACID AND SULFUR TRIOXIDE).

12. Sulfur Dioxide, Sulfurous Acid and its Salts

12.1. Sulfur Dioxide.

Physical Properties. Sulfur dioxide [7446-09-5], SO_2, is a colorless gas with a characteristic pungent, choking odor. Its physical and thermodynamic properties are listed in Table 8. Heat capacity, vapor pressure, heat of vaporization, density, surface tension, viscosity, thermal conductivity, heat of formation, and free energy of formation as functions of temperature are available (272,273), as is a detailed discussion of the sulfur dioxide−water system (274).

Liquid sulfur dioxide expands by ~10% when warmed from 20 to 60°C under pressure. Pure liquid sulfur dioxide is a poor conductor of electricity, but high conductivity solutions of some salts in sulfur dioxide can be made (275). Liquid sulfur dioxide is only slightly miscible with water. The gas is soluble to the extent of 36 volumes per volume of water at 20°C, but it is very soluble (several hundred volumes per volume of solvent) in a number of organic solvents, eg, acetone, other ketones, and formic acid. Sulfur dioxide is less soluble in nonpolar solvents (274,276,277). The use of sulfur dioxide as a solvent and reaction medium has been reviewed (275,278).

Inorganic Chemistry. Sulfur dioxide is extremely stable to heat, even up to 2000°C. It is not explosive or flammable in admixture with air. The oxidation of sulfur dioxide by air or pure oxygen is a reaction of great commercial importance and is commonly conducted at 400–700°C in the presence of a catalyst, eg, vanadium oxide. The oxidation of sulfur dioxide to sulfur trioxide for manufacture of sulfuric acid has been discussed (see SULFURIC ACID AND SULFUR TRIOXIDE). For oxidation of sulfur dioxide at low levels, eg, in smelter off-gases, various catalysts as well as chemical oxidants such as Caro's acid, H_2SO_5, are used (279). In certain sulfur dioxide recovery processes, oxidation of sulfur dioxide is carried out on activated carbon (qv), which also serves as an adsorbent for the sulfur trioxide and sulfuric acid produced (280). The oxidation of sulfur dioxide to sulfuric acid and sulfates in the atmosphere is important with regard to air pollution studies (281–283). Radicals, eg, HO, HO_2, and CH_3O_2, appear to be the principal species responsible for the homogeneous oxidation of sulfur dioxide in the atmosphere, which can occur at rates as high as 4%/h (283).

Oxidation of sulfur dioxide in aqueous solution, as in clouds, can be catalyzed synergistically by iron and manganese (284). The oxidation kinetics in aqueous slurry of calcium sulfite and sulfate with manganous sulfate catalyst have been studied (285). Ammonia can be used to scrub sulfur dioxide from gas streams in the presence of air. The product is largely ammonium sulfate formed by oxidation in the absence of any catalyst (286). The oxidation of SO_2 catalyzed by nitrogen oxides was important in the early processes for manufacture of sulfuric acid (qv). Sulfur dioxide reacts with chlorine or bromine forming sulfuryl chloride or bromide [507-16-4].

$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2$$

Reduction of sulfur dioxide to sulfur includes an industrially important group of reactions (287). Hydrogen sulfide reduces sulfur dioxide even at ambient temperature in the presence of water, but in the dry state and in the absence of a catalyst, a temperature of ~300°C is required.

$$SO_2 + 2\,H_2S \longrightarrow 3/x\,S_x + 2\,H_2O$$

This reaction is catalyzed by bauxite, and various metal sulfides. The usual catalyst is activated alumina, which also catalyzes the reduction by methane (288). Molybdenum compounds on alumina are especially effective catalysts for the hydrogen sulfide reaction (289).

The Claus process, which involves the reaction of sulfur dioxide with hydrogen sulfide to produce sulfur in a furnace, is important in the production of sulfur from sour natural gas or by-product sulfur-containing gases (see SULFUR REMOVAL AND RECOVERY).

When the Claus reaction is carried out in aqueous solution, the chemistry is complex and involves polythionic acid intermediates (131,270). A modification of the Claus process (by Shell) uses hydrogen or a mixture of hydrogen and carbon monoxide to reduce sulfur dioxide, carbonyl sulfide, carbon disulfide, and sulfur mixtures that occur in Claus process off-gases to hydrogen sulfide over a cobalt molybdate catalyst at ~300°C (290). Reformed natural gas reduces sulfur dioxide in a process developed by Asarco (291).

Reduction of sulfur dioxide by methane is the basis of an Allied process for converting by-product sulfur dioxide to sulfur (292). The reaction is carried out in the gas phase over a catalyst. Reduction of sulfur dioxide to sulfur by carbon in the form of coal has been developed as the Resox process (293). The reduction, which is conducted at 550–800°C, appears to be promoted by the simultaneous reaction of the coal with steam. The reduction of sulfur dioxide by carbon monoxide tends to give carbonyl sulfide [463-58-1] rather than sulfur over cobalt molybdate, but special catalysts, eg, lanthanum titanate, have the ability to direct the reaction toward producing sulfur (294).

With hot metals, sulfur dioxide usually forms both metal sulfides, as well as metal oxides. In aqueous solution, sulfur dioxide is reduced by certain metals or by borohydrides to dithionites.

Sulfur dioxide dissolves in water, forming a weak acid solution of sulfurous acid, H_2SO_3; however, the pure substance H_2SO_3 has never been isolated. At 101.3 kPa (1 atm) sulfur dioxide pressure, the solubility of sulfur dioxide is 18.5% at 0°C and 5.1% at 40°C. Lower solubilities are observed when other diluent gases, eg, air, are present. At 25°C, the hypothetical H_2SO_3 has a first ionization constant of 1.72×10^{-2} and a second ionization constant of 1.1×10^{-9}. At low temperatures, concentrated sulfurous acid affords a crystalline hydrate, $SO_2 \cdot 6H_2O$ [24402-69-5].

The absorption of sulfur dioxide in alkaline (even weakly alkaline) aqueous solutions affords sulfites, bisulfites, and metabisulfites. The chemistry of the interaction of sulfur dioxide with alkaline substances, either in solution, slurry, or solid form, is also of great technological importance in connection with air pollution control and sulfur recovery (25,287,295–301). Even weak bases, such as zinc oxide, absorb sulfur dioxide. A slurry of zinc oxide in a smelter can be used to remove sulfur dioxide and the resultant product can be recycled to the roaster (302).

The anaerobic reaction of sulfur dioxide with aqueous ammonia produces a solution of ammonium sulfite [10192-30-0]. This reaction proceeds efficiently, even with a gas stream containing as little as 1 wt% sulfur dioxide. The sulfur dioxide can be regenerated at a high concentration by acidulation or by stream stripping of the ammonium sulfite solution, or the sulfite can be made to precipitate and the ammonia recovered by addition of lime (303). The process can also be modified to produce ammonium sulfate for use as fertilizer (304) (see FERTILIZERS). In a variant of this process, the use of electron-beam radiation catalyzes the oxidation of sulfur dioxide in the presence of ammonia to form ammonium sulfate (305).

Organic Chemistry. The organic chemistry of sulfur dioxide, particularly as it relates to food applications, has been discussed (306). Although no reaction takes place with saturated hydrocarbons at moderate temperatures, the simultaneous passage of sulfur dioxide and oxygen into an alkane in the presence of a free-radical initiator or ultraviolet light affords a sulfonic acid, such as hexanesulfonic acid [13595-73-8]. This is the so-called sulfoxidation reaction (307):

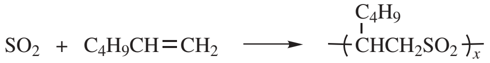
$$2\,C_6H_{14} + 2\,SO_2 + O_2 \longrightarrow 2\,C_6H_{13}SO_3H + H_2O$$

Simultaneous treatment of an alkane with sulfur dioxide and chlorine affords a sulfonyl chloride, eg, hexylsulfonyl chloride [14532-24-2], and is referred to as chlorosulfonation or the Reed reaction (307,308).

$$C_6H_{14} + SO_2 + Cl_2 \longrightarrow C_6H_{13}SO_2Cl + HCl$$

Isomer mixtures are generally obtained. Chlorosulfonation is used to produce chlorosulfonated polyethylene, a curable thermoplastic. Preformed sulfuryl chloride may also be used.

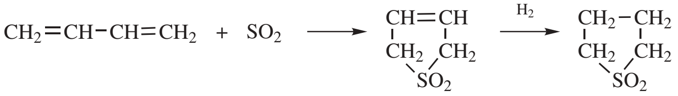
The reaction of sulfur dioxide with olefins under free-radical-catalyzed conditions produces copolymers which, in most cases, are of an alternating 1:1 type (309,310):



$$SO_2 + C_4H_9CH{=}CH_2 \longrightarrow -\!\!\left(\overset{C_4H_9}{\overset{|}{C}}HCH_2SO_2\right)\!\!\!-_x$$

Although these polymers have inadequate stability and processibility for most plastics applications, the ability to undergo scission back to the gaseous monomers has afforded some utility in fabrication of electron-beam resists for photolithography. Polybutene sulfone (311) and polyhexene sulfone (312) have been proposed for this small volume, but high value, application.

Sulfur dioxide acts as a dienophile in the Diels-Alder reaction with many dienes (313,314) and this reaction is conducted on a commercial scale with butadiene. The initial adduct, sulfolene [77-79-2] is hydrogenated to a solvent, sulfolane [126-33-0], which is useful for selective extraction of aromatic hydrocarbons from



a refinery stream and as a dipolar aprotic reaction solvent with good thermal and chemical stability. Sulfur dioxide reacts with Grignard reagents forming sulfinic acid salts.

$$2\,RMgCl + 2\,SO_2 \longrightarrow (RSO_2)_2Mg + MgCl_2$$

Other reactions of sulfur dioxide forming sulfinic acids or sulfones have been reviewed (314).

Manufacture. Combustion of Sulfur. For most chemical process applications requiring sulfur dioxide gas or sulfurous acid, sulfur dioxide is prepared by the burning of sulfur or pyrite [1309-36-0], FeS_2. A variety of sulfur and pyrite burners have been developed for sulfuric acid and for the pulp (qv) and paper (qv) industries, which produce and immediately consume ~90% of the captive sulfur dioxide produced in the United States. Information on the European sulfur-to-sulfuric acid technology (with emphasis on Lurgi) is available (315).

The production of sulfur dioxide gas by combustion of Frasch-process sulfur and sulfur recovered from natural gas or oil-refinery gases is relatively simple and is the preferred method, except in cases in which economic considerations favor the use of pyrite, such as in some European countries. For most applications, with the exception of sulfuric acid manufacture, as high a sulfur dioxide content as possible is desired. For sulfur burners utilizing air, the theoretical maximum is 21 vol% SO_2, and under satisfactory conditions 14–20 vol% can be achieved. The various sulfur burners commercially available are rated by their manufacturers as capable of producing gas in the range of 5–18 wt% sulfur dioxide. In the upper range of sulfur dioxide concentration, theoretical flame temperatures for the combustion of sulfur in air are 1200–1600°C. One kilogram of sulfur requires 1 kg of oxygen for its complete combustion. This is the amount contained in 3.35 m^3 air. The reaction produces 4500 kJ/kg (1942 Btu/lb) of sulfur dioxide from sulfur. The types of burners used are also dependent on scale, with typical usages as follows: high pressure spray (multiple units), 35,000 kg/h; multifluid atomization (multiple units), 35,000 kg/h; spinning cup (single unit), 35,000 kg/h; rotary kiln (single unit), at or $<$ 900 kg/h; and pan-type burner (single unit), at or $<$ 610 kg/h.

Large sulfuric acid plants are based on spray burners, where the sulfur is pumped at 1030–1240 kPa (150–180 psig) through several nozzles into a refractory-lined combustion chamber. An improved nozzle, resistant to plugging or fouling, has been introduced (316). The combustion chambers are typically horizontal baffle-fitted refractory-lined vessels. The largest plants in fertilizer complexes burn up to 50 t/h of sulfur.

Spinning-cup atomizers are used in some plants to provide finer atomization, allowing smaller burner chambers and easier turndown, but with the burden of added rotating equipment. Rotary kiln burners were once popular to burn lower quality sulfur, but few are still in operation. Spray burners can be operated intermittently and used at higher rates than rotary burners.

Pan and cascade burners are generally more limited in flexibility and are useful only where low sulfur dioxide concentrations are desired. Gases from sulfur burners also contain small amounts of sulfur trioxide, hence the moisture content of the air used can be important in achieving a corrosion-free operation. Continuous operation at temperatures above the condensation point of the product gases is advisable where exposure to steel (qv) surfaces is involved. Pressure atomizing-spray burners, which are particularly suitable when high capacities are needed, are offered by the designers of sulfuric acid plants.

Air-atomizing sulfur burners can use smaller combustion chambers at the expense of requiring more power to compress the air. Air is preheated in a jacket, permitting faster combustion. The combustion volume can be as low as 0.085 m^3 (3 ft^3) to burn 900 kg/d of sulfur (317). These burners can deliver high strength gases of 17–19 vol% SO_2 and are used in plants that produce liquid SO_2 and in pulp mills. Enriched air–oxygen can be used as the atomizing fluid in sprays that use external mixing at the point of atomization. A particularly efficient and clog-resistant spray nozzle uses a combination of air atomization and effervescent atomization (317).

The spinning-cup sulfur burner is suitable for very large capacities, ie, up to 39 t/h of sulfur in a single spinning cup. It is similar to spinning-cup oil burners, except that it is modified to prevent solidification of sulfur. The spinning cup provides centrifugal motion to the sulfur, which is then atomized by a flow of air in an annular space surrounding the cup. This burner also sprays the sulfur into a brick-lined combustion chamber.

Lurgi, Monsanto, and others have developed substoichiometric sulfur burners. The use of pure or enriched oxygen for burning sulfur is advocated by various oxygen suppliers, who provide burner and chamber designs for this purpose. With the improvements in hollow-fiber separation of air, the economic advantage of enriched oxygen for burning sulfur is increasing. Submerged combustion of molten sulfur with oxygen has been in use since 1989, and fits well into refinery Claus unit operation (318).

Other burners are used for low capacity operations. A cascade or checker burner, in which molten sulfur flows down through brick checkerwork countercurrent to a flow of air, is used in small units with a sulfur trioxide converter to condition gases entering electrostatic precipitators at boiler plants operating on low sulfur coal. A small pan burner, which is fed with solid, low carbon sulfur, is used to produce sulfur dioxide for solution in irrigation water to control the pH and maintain porosity in the soil. The same type of burner is used to disinfect wastewater; in this case sulfur dioxide is used instead of chlorine.

It has been proposed that the excess sulfur production from sour gas and tar sands be burned to sulfur dioxide for energy recovery (avoiding carbon dioxide production from carbon-based fuels) and the sulfur dioxide reinjected into sour gas strata. This process is under study in Alberta (319). A very high purity sulfur dioxide can be produced by the relatively recent Calabrian SO_2 Clean process where in a specially designed burner, molten sulfur is burned by pure oxygen to produce 99.99% pure SO_2 (320). This is convenient for the user because no moisture, sulfur trioxide or inert gases are involved. Calabrian also produces and ships high purity SO_2 made by this process on a large scale.

Burning Pyrites. This source of sulfur dioxide for fertilizer production has recently been replaced at Europe's largest acid plant in Spain by direct burning of sulfur (321), which now has a cost advantage.

The burning of pyrite is considerably more difficult to control than the burning of sulfur, although many of the difficulties have been overcome in mechanical pyrite burners. A number of plants burn pyrite or zinc, lead, copper, and nickel sulfides in fluid-bed roasters. The pyrite is fed onto a grate where it and its calcines are kept as a fluid by an upward flow of air through openings in the grate (see FLUIDIZATION). Use of oxygen instead of air in a specially designed fluidized-bed apparatus makes possible the manufacture of high strength sulfur dioxide from sulfide ore (322).

A technique known as flash roasting was developed in the 1920s. Finely ground pyrites or other sulfide ores fall through a chamber in which air is introduced countercurrently from the bottom. The particles burn at 1000–1100°C yielding sulfur dioxide free of sulfur trioxide at a concentration suitable for making sulfuric acid or for sulfite pulping (323).

A basic research study on combustion of sulfur led to the postulation that sulfur trioxide may actually be the primary combustion product and that sulfur dioxide may then be produced by the further reaction of sulfur trioxide with sulfur vapor in the oxygen-deficient region of the flame (324).

Recovery from Flue Gases. Recovery of sulfur dioxide from flue gases has been described (25,112,287). The stack gas from smelting often contains sufficient sulfur dioxide (~ 6 wt%) for economic conversion to sulfuric acid; the lower concentration in power plant stack gases generally requires some method for concentrating the sulfur dioxide.

Production from Oleum. Production of SO_2 from oleum was developed at Stauffer Chemical Company and is used commercially to produce liquid sulfur dioxide. It can be integrated with an existing oleum operation or with a concentrated sulfuric acid-consuming operation.

$$2\,SO_3 + S^0 \longrightarrow 3\,SO_2$$

A flow diagram of the plant is shown in Fig. 1. Approximately 30 wt% oleum is pumped into a reboiler; *2*, and SO_3 is evolved. The resultant 20 wt% oleum is returned to the oleum towers of an acid plant. For heat conservation, the oleum streams are interchanged in a heat exchanger, *1*. The SO_3 stream passes through molten sulfur in reactor *3*, where the reaction takes place, and molten sulfur is continuously fed to reactor *3*. Periodically, sludge is withdrawn from the reactor; this occurs every six to eight months if bright sulfur is used. The SO_2 vapors pass through a sulfuric acid tower for removal of trace SO_3. Cooling, *9*; gas cleaning, *10*; compressing, *11*; and water condensation, *13*, complete the process of producing liquid SO_2 for storage. The reactor, *3*, is cooled and/or heated for startup by a closed-water circulation loop, *4–6*. The sulfur dioxide produced is 99.99% pure. Rhodia operates commercial plants of this type. Development of gas-cleaning techniques and proper economical materials of construction has resulted in over 96% on-stream time.

The NEAT SO_2 process has been developed by Navdeep Industrial and Technical Services, India, wherein the oxidation of sulfur by sulfur trioxide is carried out at 50–110°C in a pressurized water-jacketed continuous reactor (320). This process fits well into an existent sulfuric acid plant where sulfur trioxide is available, and it can be adapted to dispose of sulfur filter cake, a problematic waste generated in sulfuric acid plants.

Another method of handling sulfur dioxide is to collect, store and ship it in an amine solvent, the patented SO_2SAFE system, from which it can be regenerated by heating (320,326). This is an extension of the CANSOLV scrubbing system Safety advantages must be balanced off against the cost of transport. Another version of the regenerable scrubber approach, the LABSORB process, uses aqueous sodium phosphate (327).

Production from Spent Sulfuric Acid. Spent sulfuric acid recovered from petrochemical and refinery processes can be fed to a high temperature furnace at 870–1260°C, where it is transformed into sulfur dioxide, water, and oxidative destruction of the contaminants. After suitable scrubbing and drying, the gases are passed to a conventional contact sulfuric acid plant (328). Improved regeneration processes use oxygen to gain higher yields, lower energy consumption and less byproduct nitrogen oxide production (329).

Corrosivity. Almost all common materials of construction are resistant to commercial dry liquid sulfur dioxide, dry sulfur dioxide gas, and hot sulfur dioxide gas containing water at above the dew point (330,331). These include cast iron, carbon steel, copper, brass, and aluminum. Where hot gases or hot solutions are involved, the temperature resistance, particularly for plastics and resins, and the resistance to thermal shock, particularly for ceramic, glass, and stone, should be taken into account. The latter materials are inert to wet gas, sulfurous acid, and sulfite solutions. Carbon, graphite, and impregnated carbon are suitable for practically all types of sulfur dioxide service. Lead is also resistant to sulfur dioxide and sulfites under most conditions. Aluminum is resistant under a variety of conditions and is favored in some food-industry applications involving wet sulfur dioxide. Organic coatings are generally resistant but may fail if gas diffusion through the film is appreciable. Among the organic materials, hard rubber has been satisfactory in sulfurous acid at moderate temperatures, and butyl rubber may perform similarly.

Iron, steel, nickel, copper–nickel alloys, and Inconel Ni–Cr–Fe are satisfactory for dry or hot sulfur dioxide, but are readily corroded below the dew point or by wet sulfur dioxide gas, sulfurous acid, and sulfites. Inconel is especially resistant to very hot sulfur dioxide gas. Metals best suited to a wide variety of wet, dry, and hot sulfur dioxide, sulfurous acid, and sulfite service are nickel–chromium alloys, eg, Worthite and Durimet 20, and several of the austenitic stainless steels. Type 304 may be satisfactory for mild conditions, but types 316 and 317 are usually required for more severe applications at high temperatures. When sulfuric acid is also present, the 20-grade stainless steels may be needed. Crucible SC-1 stainless steel is said to be useful for sulfur dioxide scrubbers (332).

Liquid sulfur dioxide discolors iron, copper, and brass at ~ 300 ppm moisture and produces light scale at ~ 0.1 wt% moisture and serious corrosion at ~ 0.2 wt% or higher moisture content. Copper and brass can be used to handle wet sulfur dioxide where some corrosion can be tolerated, or where the moisture level is low. Wooden tanks are widely used for sulfurous acid preparation, handling, and storage. Sulfite pulp digestors are made of steel lined with acid-resistant brick.

Corrosion by atmospheric sulfur dioxide should be considered in the development and evaluation of protective coatings (333,334). Sulfur dioxide and sulfuric acid therefrom are highly damaging to carbonate building stones (335).

Shipment and Storage. Liquid sulfur dioxide is commonly shipped in North America using 55- and 90-t tank cars, 20-ton tank trucks, 1-ton cylinders, and 150-lb cylinders. Cylinders made of specified steel are affixed with the green label for nonflammable gases. The DOT classification is Poison Gas, Inhalation Hazard. Purchasers of tank-car quantities are required to have adequate storage facilities for prompt transfer.

All shipping containers for liquid sulfur dioxide are arranged so that withdrawal or transfer of the contents can be effected either as a gas or as a liquid. In general, the pressure of the sulfur dioxide in its container is used for the transfer. The most convenient method for attaining the required pressure differential in the case of cylinders and drums is heating. Because these containers are equipped with fusible plugs, it is recommended that the temperature never be allowed to exceed 52°C either in storage or during heating for transfer. In order to minimize the danger of a container of sulfur dioxide becoming full of liquid and failing as a result of the development of hydrostatic pressure with rising temperature, the maximum allowable sulfur dioxide capacity by weight of any container has been set by DOT at 1.25 times the water capacity by weight. It is common practice to fill containers to only 1.15 times the water capacity.

Economic Aspects. A market profile of sulfur dioxide as of January 2004 is available (336). Merchant sulfur dioxide is produced by North American manufacturers; the total capacity excluding captive production in the United States is in the area of 176,000–300,000 short tons (numbers vary with source). The largest producer in the United States may be Rhodia (from sulfur trioxide reduction by sulfur, ie, spent sulfuric acid regeneration). There is also a larger captive production by sulfuric acid producers. In the 2004 report, list price for merchant sulfur dioxide was given as \$230/ton and spot pricing as \$130–150/ton. No growth of merchant sulfur dioxide was projected since large users tend to burn sulfur onsite. The use in water treatment to reduce residual chlorine is expected to decline in areas that move away from water chlorination.

Uses (besides captive use for making sulfuric acid) are estimated (336) to be manufacture of hydrosulfites (25%), other chemicals, 20%; pulp and paper, 15%; food and agriculture (mainly corn syrup and other sugar processing, preservation of fruits, vegetables wine and beer), 15%; water and waste treatment, 10%; metal and ore refining (as a sulfide depressant in flotation), 6%; oil recovery and refining (as oxygen scavenger to retard corrosion), 4%; and miscellaneous, including sulfonation of oils and as a reducing agent or antioxidant, 5% (336–338). The pulp and paper industry is expected to have the greatest growth because of increased paper recycling, requiring bleaching.

Grades and Specifications. The main grade of liquid sulfur dioxide is known as the technical, industrial, or commercial grade. This grade contains a minimum of 99.98 wt% sulfur dioxide and is a water-white liquid free of sulfur trioxide and sulfuric acid. It contains only a trace at most of nonvolatile residue. Its most important specification is the moisture content, which is generally set at 100 ppm maximum. The only other grade sold is the refrigeration grade of liquid sulfur dioxide, a premium grade having the same purity and specifications as the industrial grade, except for the moisture content, which is specified as 50 ppm maximum. At least one manufacturer sells a single grade for which specifications have been established as follows: color, APHA 25 max; nonvolatile residue, 25 ppm max; and moisture, 50 ppm max.

Analytical Methods. The official NIOSH recommended method for determining sulfur dioxide in air consists of drawing a known prefiltered volume of air through a bubbler containing hydrogen peroxide, thus oxidizing the sulfur dioxide to sulfuric acid. Isopropyl alcohol is then added to the contents in the bubbler and the pH of the sample is adjusted with dilute perchloric acid. The resultant solution is then titrated for sulfate with 0.005 M barium perchlorate, and Thorin is used as the indicator; in the range 6.6–26.8 mg/m^3 this method is useful for compliance with the OSHA standard (339).

A method suitable for analysis of sulfur dioxide in ambient air and sensitive to 0.003–5 ppm involves aspirating a measured air sample through a solution of potassium or sodium tetrachloromercurate, with the resultant formation of a dichlorosulfitomercurate. Ethylenediaminetetraacetic acid (EDTA) disodium salt is added to this solution to complex heavy metals that can interfere by oxidation of the sulfur dioxide. The sample is also treated with 0.6 wt% sulfamic acid to destroy any nitrite anions. Then the sample is treated with formaldehyde and specially purified acid-bleached rosaniline containing phosphoric acid to control pH. This reacts with the dichlorosulfitomercurate to form an intensely colored rosaniline–methanesulfonic acid. The pH of the solution is adjusted to 1.6 ± 0.1 with phosphoric acid, and the absorbance is read spectrophotometrically at 548 nm (340).

The Reich test is used to estimate sulfur dioxide content of a gas by measuring the volume of gas required to decolorize a standard iodine solution (341). Equipment has been developed commercially for continuous monitoring of stack gas by measuring the near-ultraviolet (uv) absorption bands of sulfur dioxide (342–344). The determination of sulfur dioxide in food is conducted by distilling the sulfur dioxide from the acidulated sample into a solution of hydrogen peroxide, followed by acidimetric titration of the sulfuric acid thus produced (345). Analytical methods for sulfur dioxide have been reviewed (346).

Interest in trace determination of sulfur dioxide in the atmosphere has led to a number of instrumental methods, such as chemiluminescence in a hydrogen-rich flame (347), matrix isolation and Fourier transform infrared (FTir) spectroscopy (348), colorimetric determination (349), conductimetric sensing after passage through a special membrane (350), and high pressure chemical ionization mass spectrometry (351). Continuous monitoring methods have been compared using uv, ir, and electrochemical methods (352,353). Other continuous monitoring means have been described using chemiluminescence (354) and solid electrolyte sensors, said to be rugged enough for stack gas monitoring (355). In continuous monitoring as much as 30% of the sulfur dioxide may be lost in condensed moisture (356).

Health, Safety, and Environmental Factors. Sulfur dioxide has only a moderate acute toxicity (357). A review of its toxicology is available (357,358).

The lowest published human lethal concentration is 1000 ppm for 10 months. The lowest published human toxic concentration by inhalation is 3 ppm for 5 days or 12 ppm for 1 h. The lowest published human lethal concentration is 3000 ppm for 5 months. In solution (as sulfurous acid), the lowest published toxic dose is 500 μg/kg causing gastrointestinal disturbances. Considerable data are available by other modes of exposure and to other species; NIOSH standards are a time-weighted average of 2 ppm and a short-term exposure limit of 5 ppm (357).

Sulfur dioxide is a severe eye irritant (eye irritation level 10 ppm) and skin irritant in humans (358–360). Inhalation of vapor may lead to irritation of the respiratory tract, cough, sore throat, increased salivation, nausea, vomiting, bronchoconstriction, chronic respiratory disease, and pulmonary edema. Exposure to very high concentrations may induce acute and chronic bronchitis, chemopneumonia, asphyxia, and death. Respiratory effects have been attributed to workplace exposure. Concentrations even as low as 2 ppm can have a respiratory irritant, choking, and sneeze/cough inducing effect, but some persons can acclimatize to 20–30 ppm. Human subjects have reported 50 ppm to be intolerable. ACGIH has set a threshold limit value-time weighted average of 2 ppm (5.2 mg/m^3) and the threshold limit value: short-term exposure limit (TLV-STEL) of 5 ppm (13 mg/m^3) due to its irritation potential (361). Additionally, NIOSH has assigned an immediately dangerous to life or health (IDLH) concentration of 100 ppm.

Lung tumors were reported in mice following long-term inhalation exposure, but sulfur dioxide is not classified as a human carcinogen (361).

Sulfur dioxide shows some mutagenic effects in microorganisms and fruit flies. Human lymphocyte DNA damage has been observed. It is an equivocal tumorigenic agent by RTECS criteria (234,357). Sulfur dioxide occurs in industrial and urban atmospheres at 1 ppb−1 ppm and in remote areas of the earth at 50−120 ppt. Plants and animals have a natural tolerance to low levels of sulfur dioxide (362). Some plants have a detoxification route for sulfur dioxide. Living species have had exposure to sulfur dioxide over geologic times from natural sources that include volcanoes and volcanic vents, decaying organic matter, and solar action on seawater (363,364). Sulfur dioxide is believed to be the main sulfur species produced by oxidation of dimethyl sulfide that is emitted from the ocean.

The status of knowledge regarding source−receptor relationships, climatological factors, and atmospheric chemistry as a background for regulatory policy has been reviewed (365). The 1990 Clean Air Act Amendments are intended to cut annual sulfur dioxide emissions 40% from 1980 levels, and thus minimize the potential effects of acid rain, which can occur even at great distances from the source. The program formulated under this legislation allows market-based trading of emission allowances and flexibility in choice of technologies to reduce emissions, so as to ameliorate lake and stream acidification and damage to plants, structures, and humans. Estimated emissions of sulfur dioxide in the United States declined from 25.7×10^6 t in 1980 to $\sim 20 \times 10^6$ t in 2004, $\sim$65% of which is attributable to electric utilities according to the EPA. Downward trends in atmospheric sulfate have been noted. However, acidification continues to effect sensitive forest, soil, and aquatic ecosystems. Human health data appear inconclusive at other than extreme levels. Regulatory action to limit sulfur emissions has already had a significant impact on the capital and operating costs of power generation (qv), the selection of fuel, and the coal mining, gas, and petroleum industries. The benefits of proposed regulation must be weighed against high costs and economic disruptions.

Beneficial and Harmful Effects on Plants. At low levels, sulfur dioxide in the atmosphere is not harmful to crops, but damage can occur at excessive levels (366–370). Crops differ greatly in their sensitivity. The physicological, biochemical and molecular effects of sulfur dioxide in plants have been studied (371).

Forest damage attributed to acid rain is often cited, but the observed symptoms seem to have multiple causes and the contribution of sulfur acids is unspecified. The sulfur in precipitation is, up to a point, beneficial to plant growth because sulfur is an essential nutrient. Lessening the sulfur content of the atmosphere requires that supplementary sulfur be provided in fertilizer to some crops; some crops already require supplementary sulfur. Sulfur dioxide itself has been found useful in drip irrigation systems (372,373) and in calcareous soils (368). Small field generators have been developed for this purpose.

Sulfur Dioxide Emissions and Control. A substantial part of the sulfur dioxide in the atmosphere is the result of burning sulfur-containing fuel, notably coal, and smelting sulfide ores. Methods for controlling sulfur dioxide emissions have been reviewed (374–376) (see also AIR POLLUTION CONTROL METHODS; COAL CON-

VERSION PROCESSES, CLEANING AND DESULFURIZATION; EXHAUST CONTROL, INDUSTRIAL; SULFUR REMOVAL AND RECOVERY).

Some newer methods of adsorbing sulfur dioxide to prevent emissions involve use of supported magnesia or hydrotalcite (327). Reviews of sulfur dioxide scrubbing technologies are available (377–379).

Uses. The dominant use of sulfur dioxide is as a captive intermediate for production of sulfuric acid. There is also substantial captive production in the pulp and paper industry for sulfite pulping, and it is used as an intermediate for on-site production of bleaches, eg, chlorine dioxide or sodium hydrosulfite (see BLEACHING AGENTS SURVEY). There is a substantial merchant market for sulfur dioxide in the paper and pulp industry. Sulfur dioxide is used for the production of chlorine dioxide at the paper (qv) mill site by reduction of sodium chlorate in sulfuric acid solution and also for production of sodium dithionite by the reaction of sodium borohydride with sulfur dioxide (380). This last application was growing rapidly in North America as of the late 1990s.

A smaller, but important, use for sulfur dioxide is for stabilization of pulp (qv) brightness after hydrogen peroxide bleaching of mechanical pulps. Sulfur dioxide neutralizes the alkalinity and destroys any excess hydrogen peroxide, which if left in the pulp would cause it to lose brightness.

In food processing (qv), sulfur dioxide has a wide range of applications (381,382) as a fumigant, preservative, bleach, and steeping agent for grain and dried fruit. Because of the sensitivity of some persons to sulfur dioxide, it (also its salts) has been banned for use on fresh produce by the U.S. Food and Drug Administration (FDA). In the manufacture of wine (qv), a small amount of sulfur dioxide is added to destroy bacteria, molds, and wild yeasts without harming yeasts needed for the desired fermentation. Wine casks are also sterilized by sulfur dioxide. The formation of nitrosamines in beer is prevented by sulfur dioxide treatment in the malting process (383). In molasses manufacture, sugar refining, and soy protein processing, sulfur dioxide is used for bleaching as well as for the prevention of microbial growth (384). In making high fructose corn syrups, sodium bisulfite from sulfur dioxide is added to the enzymatic isomerization step to prevent undesired microbial action. In the earlier stages, where corn is steeped in preparation to wet milling, a 0.1–0.2 wt% sulfur dioxide solution is used to swell and soften kernels and prevent growth of microorganisms. Sulfur dioxide is used throughout corn syrup processing to prevent microbial growth and retard nonenzymatic development of color by the Maillard reaction (see FOOD PROCESSING; SYRUPS).

The FDA Center for Food Safety and Applied Nutrition (CFSAN) studies sulfur dioxide in their program for Priority-based Assessment of Food Additives (PAFA). Sulfur dioxide is cited in 21CFR172.892 as a food additive permitted for direct addition to food for human consumption when used as a bleach treatment for food starch not to exceed 0.05%. Also in 21CFR 182.3862, this substance is generally recognized as safe (GRAS) when used in accordance with good manufacturing practice, except that it cannot be used in meats, in food recognized as a source of vitamin B1, on fruits or vegetables intended to be served raw to consumers or sold raw to consumers, or to be presented to consumers as fresh.

In water treatment, sulfur dioxide is often used to reduce residual chlorine from disinfection and oxidation (385). This technology is used in potable water treatment, in sewage treatment, and especially in industrial wastewater treatment (see WATER, INDUSTRIAL WATER TREATMENT; WATER, MUNICIPAL WATER TREATMENT; WATER, SEWAGE). Although sodium metabisulfite [7681-57-4] and sodium sulfite [7757-83-7] may be used, the use of liquid sulfur dioxide has convenience and cost advantages and lends itself to automation. Therefore, the larger plants tend to use sulfur dioxide rather than sulfite or bisulfite salts. Sulfur dioxide is also employed as a reducing agent for conversion of chromates to less toxic chromic compounds in plating-shop effluents.

In petroleum technology, sulfur dioxide, sodium bisulfite, or sodium sulfite are used as oxygen scavengers (386). This use is particularly important in secondary and tertiary oil recovery processes involving flooding of underground oil formations using water or aqueous solutions (see ENHANCED OIL RECOVERY). To prevent corrosion in piping and storage systems it is important to lower the oxygen concentration of the water to 50–100 ppb. The rate of oxygen reduction is increased by adding a cobalt compound as catalyst and maintaining a pH of 8.5–10 (387). Sulfur dioxide and sodium sulfites are also used in oil refining and other industrial processes, notably in boiler waters, as oxygen scavengers. Basic studies have been done on the catalysis of sulfite or bisulfite oxidation (388,389).

Another sulfur dioxide application in oil refining is as a selective extraction solvent in the Edeleanu process (390), wherein aromatic components are extracted from a kerosene stream by sulfur dioxide, leaving a purified stream of saturated aliphatic hydrocarbons that are relatively insoluble in sulfur dioxide. Sulfur dioxide acts as a cocatalyst or catalyst modifier in certain processes for oxidation of *o*-xylene or naphthalene to phthalic anhydride (391,392).

In mineral technology, sulfur dioxide and sulfites are used as flotation depressants for sulfide ores. In electrowinning of copper from leach solutions from ores containing iron, sulfur dioxide prereduces ferric to ferrous ions to improve current efficiency and copper cathode quality. Sulfur dioxide also initiates precipitation of metallic selenium from selenous acid, a by-product of copper metallurgy (393).

In kaolin (clay) processing, sulfur dioxide reduces colored impurities, eg, iron compounds. In the bromine industry, sulfur dioxide is used as an antioxidant in spent brine to be reinjected underground. In agriculture, especially in California, sulfur dioxide is used to increase water penetration and the availability of soil nutrients by virtue of its ability to acidulate saline–alkali soils (394). It is also useful for cleaning ferric and manganese oxide deposits from tile drains (395).

In magnesium casting, sulfur dioxide is employed as an inert blanketing gas. Another foundry application is as a rapid curing catalyst for furfuryl resins in cores. Surprisingly, in view of the many efforts to remove sulfur dioxide from flue gases, there are situations where sulfur dioxide is deliberately introduced. In power plants burning low sulfur coal and where particulate stack emissions are a problem, a controlled amount of sulfur dioxide injection may improve particulate removal.

Sulfur dioxide is useful as a solvent for sulfur trioxide in sulfonation reactions; eg, in the large-scale production of alkylbenzenesulfonate surfactant (396).

A newer use for sulfur dioxide is in cyanide detoxification in connection with cyanide leaching of precious metals from mine dumps.

13. Sulfur Oxygen Acids and Their Salts

Sulfuric acid, H_2SO_4, the most important commercial sulfur compound (see SULFURIC ACID AND SULFUR TRIOXIDE), and peroxymonosulfuric acid [7722-86-3] (Caro's acid), H_2SO_5, are discussed elsewhere (see PEROXIDES AND PEROXIDE COMPOUNDS, INORGANIC OXIDES). The lower valent sulfur acids are not stable species at ordinary temperatures. Dithionous acid [15959-26-9], $H_2S_2O_4$, sulfoxylic acid [20196-46-7], H_2SO_2, and thiosulfuric acid [13686-28-7], $H_2S_2O_3$ are unstable species. A discussion of efforts to isolate and characterize the unstable sulfur acids is given (397).

13.1. Sodium Sulfite.

Physical Properties. Anhydrous sodium sulfite [7757-83-7], Na_2SO_3, is an odorless, crystalline solid and most commercial grades other than by-product materials are colorless or off-white (398–401). It melts only with decomposition. The specific gravity of the pure solid is 2.633 (15.4°C). Sodium sulfite is quite soluble in water. It has a maximum solubility of 28 g/100 g sol at 33.4°C; at higher and lower temperatures, it is less soluble in water. Below this temperature, the heptahydrate crystallizes; above this temperature, the anhydrous salt crystallizes. Sodium sulfite is soluble in glycerol, but insoluble in alcohol, acetone, and most other organic solvents.

Chemical Properties. Anhydrous sodium sulfite is stable in dry air at ambient temperatures or at 100°C, but in moist air it undergoes rapid oxidation to sodium sulfate [7757-82-6]. On heating to 600°C, sodium sulfite disproportionates to sodium sulfate and sodium sulfide [1313-82-2]. Above 900°C, the decomposition products are sodium oxide and sulfur dioxide. At 600°C, it forms sodium sulfide upon reduction with carbon (399).

Aqueous solutions of sodium sulfite are alkaline and have a pH of ~9.8 at 1 wt%. The solutions are oxidized readily by air. The redox potential is a function of pH, as would be expected from the following equation:

$$SO_3^{2-} + 2\,OH^- \longrightarrow SO_4^{2-} + H_2O + 2\,e^- \qquad E^0 = +0.90\ V$$

Although the usual product of oxidation of sulfite by air is sulfate, at high pH substantial amounts of the strong oxidant Na_2SO_5 can form (402).

Sodium sulfite undergoes addition of sulfur to form sodium thiosulfate. At acidic pH, the chemistry of sodium sulfite is that of bisulfite, metabisulfite, and sulfur dioxide.

Manufacture. In a typical process, a solution of sodium carbonate is allowed to percolate downward through a series of absorption towers through which sulfur dioxide is passed countercurrently. The solution leaving the towers is chiefly sodium bisulfite of typically 27 wt% combined sulfur dioxide content. The solution is then run into a stirred vessel where aqueous sodium carbonate or sodium hydroxide is added to the point where the bisulfite is fully converted to sulfite. The solution may be filtered if necessary to attain the required product grade. A pure grade of anhydrous sodium sulfite can then be crystallized $> 40^\circ$C because the solubility decreases with increasing temperature.

In a patented process, a stirred suspension of sodium sulfite is continuously treated with aqueous sodium hydroxide and a sulfur dioxide-containing gas at 60–85°C, and 96% pure anhydrous sodium sulfite is removed by filtration (403). In another continuous one-step process, substantially anhydrous sodium carbonate and sulfur dioxide are concurrently introduced into a saturated solution of sodium sulfite at pH 6.5–7.6 and $> 35^\circ$C with continuous removal of anhydrous sodium sulfite by filtration (404).

Various processes have been disclosed wherein moist solid sodium pyrosulfite [7681-57-4] is stirred in a steam-heated vessel with sodium carbonate. The exothermic reaction at 80–110°C results in the drying of the product. A lower grade of sodium sulfite is produced commercially in the United States by Indspec Chemical Corp. as a by-product of the sulfonation–caustic cleavage route to resorcinol (400).

Shipment and Storage. Anhydrous sodium sulfite is supplied in 22.7- and 45.4-kg moistureproof paper bags or 45.4- and 159-kg fiber drums. Most sodium sulfite is shipped by rail in hopper cars. Sodium sulfite should be protected from moisture during storage. When dry it is quite stable, but when wet it is oxidized by air.

Economic Aspects. According to U.S. data from 2002, sodium sulfite is produced for merchant sales by General Chemical at ~36,000-t capacity (Claymont, Del.), Calabrian Corp. (Port Netches, Tex.), Solvay at ~55,000-t capacity (Green River, Wy.; mostly anhydrous grade), Olympic at about 8,000-t capacity (Tacoma, Wash., 20% solution and food grade only), and Southern Ionics (three plants in Gulf region, anhydrous grade only). Indspec (Petrolia, Pa.) makes sodium sulfite at ~50,000-t capacity as a coproduct of resorcinol manufacture by the benzenedisulfonic acid route; this off-color product is mostly used in pulp and paper. There are other large (mostly captive) producers; many pulp mills produce their own sulfite and try to recycle as much as possible. Uses for sodium sulfite are 60% pulp and paper; water treatment, 15%; photography, 10%; and miscellaneous, including textile bleaching, food, chemical intermediates, ore flotation, and mineral recovery, 15%. Some growth is expected as a reductant for hydrogen peroxide in nonchlorine bleaching of pulp (qv). The price for the technical-grade solid sodium sulfite in 2005 was $0.26/lb (405,406). Exports have become significant in recent years.

Grades and Specifications. The commercial grades of sodium sulfite available in the United States are (*1*) photographic grade: white crystalline material, typically 97.0 wt% minimum Na_2SO_3 assay, 0.5 wt% maximum insoluble matter, 0.15 wt% maximum alkalinity as Na_2CO_3, 20 ppm maximum iron, 20 ppm maximum heavy metals (as Pb), 0.01 wt% maximum thiosulfate (as $S_2O^{2-}{}_3$); (*2*) anhydrous technical grade: white granular material, typically 95.0–97.5 wt% Na_2SO_3 minimum assay; (*3*) anhydrous *Food Chemicals Codex* grade: 95 wt% minimum (typically 98.6 wt%) Na_2SO_3 assay, 3 ppm mixture arsenic, 10 ppm maximum heavy metals (as Pb), 30 ppm maximum selenium; (*4*) anhydrous technical (by-product) grade: pink to red-brown powder, 91 wt% Na_2SO_3 minimum, 5 wt% sodium sulfate, and ~3 wt% sodium carbonate (used in sulfite pulping and oxygen scavenging from boiler and process water); and

(*5*) aqueous solution: 22 wt% minimum Na_2SO_3, pH 8.8, specific gravity (25/25°C) 1.27. The aqueous solution is a convenient form for use under conditions, where there are no facilities for handling and dissolving solid salt (398–401).

Analytical Methods. A classical and still widely employed analytical method is iodimetric titration. This is suitable for determination of sodium sulfite, eg, in boiler water (407). Standard potassium iodate–potassium iodide solution is commonly used as the titrant with a starch or starch-substitute indicator. Sodium bisulfite occurring as an impurity in sodium sulfite can be determined by addition of hydrogen peroxide to oxidize the bisulfite to bisulfate, followed by titration with standard sodium hydroxide (346).

Health and Safety Factors. Although sodium sulfite has no detectible odor, its dust and solutions are irritating to the skin, eyes, and mucous membranes. The ingestion of sodium sulfite causes gastric irritation resulting from the liberation of sulfurous acid. Large doses can cause violent colic and diarrhea as well as disturbance of the circulatory and nervous system. Sodium sulfite has an acute oral LD_{50} (mouse) of 820 mg/kg. It is weakly mutagenic in some test microorganisms and mammalian cells. There is inadequate evidence of any carcinogenicity (234). Some persons are very sensitive to sulfites in food and drink, so that the FDA has set limits on its use as a preservative (406).

Uses. Many of the applications of sodium sulfite are also applications in which sulfur dioxide may be used, and are discussed under the latter compound.

Pulp Manufacture. Sodium sulfite is utilized in neutral semichemical pulping, acid sulfite pulping, and some kraft pulping processes (408). Many pulp mills prepare their own sulfite and recycle as much as possible, but use of merchant sodium sulfite by pulp mills is substantial. New developments in thermomechanical pulping make use of sulfite pretreatment; various versions have been described (409). Other advantageous versions of sulfite and kraft pulping, particularly a new hybrid process, have been recently described (410).

Much of the by-product sodium sulfite from resorcinol manufacture goes into pulp applications, as well as a substantial fraction of the lower assay manufactured sodium sulfite.

Water Treatment. Sodium sulfite is an agent in the reduction of chlorine or oxygen in water. Dissolved oxygen in boiler water tends to enhance pitting and other types of corrosion. In boilers operated at < 4.82 MPa (700 psi), a residual concentration of 30 ppm of sodium sulfite is generally effective. Catalytic amounts of cobalt are often added to accelerate the reaction of oxygen with sulfite (386,387) (see WATER, INDUSTRIAL WATER TREATMENT).

In waterflooding of oil fields, oxygen dissolved in the water can contribute to pitting of pipes and clogging of injection wells and the oil-bearing rock with iron corrosion products. A residual concentration of ~ 10 ppm sodium sulfite is usually effective in preventing these problems. Sodium sulfite is also used to remove oxygen from drilling muds (see PETROLEUM COMPOSITION; DRILLING FLUIDS).

In removing excess free chlorine from municipal or industrial water, from pulp bleaching plant vent gas scrubbers, and from wastewater, sodium sulfite competes with bisulfite, sulfur dioxide or thiosulfate. The considerations involved in choosing the reductant have been reviewed (411). Other commercial applications of sodium sulfite in wastewater treatment include the reduction of hexavalent chromium to the less toxic Cr^{3+} salts, as well as the precipitation of silver and mercury.

Photography. Sodium sulfite is useful as a reducing agent in certain photographic fixing baths, developers, hardeners, and intensifiers (401). However, the principal use is as a film preservative and discoloration preventative (see PHOTOGRAPHY).

Miscellaneous. In ore flotation, sodium sulfite functions as a selective depressant. In textile processing, sodium sulfite is used as a bleach for wool (qv) and polyamide fibers and as an antichlor after the use of chlorine bleach. Synthetic applications of sodium sulfite include production of sodium thiosulfite by addition of sulfur and the introduction of sulfonate groups into dyestuffs and other organic products. Sodium sulfite is useful as a scavenger for formaldehyde in aminoplast-wood compositions, and as a buffer in chrome tanning of leather.

13.2. Sodium Bisulfite. Sodium bisulfite, $NaHSO_3$, exists in solution, but is not a stable compound in the solid state. The anhydrous sodium bisulfite of commerce consists of sodium metabisulfite, $Na_2S_2O_5$. Aqueous sodium bisulfite solution, having specific gravity 1.36 and containing the equivalent of 26–27 wt% SO_2, is a commercial product. Its price in 2005 is ~ $0.32/lb. Most of the uses are the same as for sodium sulfite or sulfur dioxide.

13.3. Sodium Metabisulfite. *Physical Properties.* Sodium metabisulfite (sodium pyrosulfite, sodium bisulfite (a misnomer)), $Na_2S_2O_5$, is a white granular or powdered salt (specific gravity 1.48) and is storable when kept dry and protected from air. In the presence of traces of water, it develops an odor of sulfur dioxide and in moist air it decomposes with loss of part of its SO_2 content and by oxidation to sodium sulfate. Dry sodium metabisulfite is more stable to oxidation than dry sodium sulfite. At low temperatures, sodium metabisulfite forms hydrates with 6 and 7 mol of water. The solubility of sodium metabisulfite in water is 39.5 wt% at 20°C, 41.6 wt% at 40°C, and 44.6 wt% at 60°C (412). Sodium metabisulfite is fairly soluble in glycerol and slightly soluble in alcohol.

Chemical Properties. The chemistry of sodium metabisulfite is essentially that of the sulfite–bisulfite–metabisulfite–sulfurous acid system. The relative proportions of each species depend on the pH. The pH of a sodium bisulfite solution obtained by dissolving 10 wt% sodium metabisulfite in water at 20°C is 4.9; at 30 wt%, the pH is 4.4.

Manufacture. Aqueous sodium hydroxide, sodium bicarbonate, sodium carbonate, or sodium sulfite solution are treated with sulfur dioxide to produce sodium metabisulfite solution. In one operation, the mother liquor from the previous batch is reinforced with additional sodium carbonate, which need not be totally in solution, and then is treated with sulfur dioxide (413,414). In some plants, the reaction is conducted in a series of two or more stainless steel vessels or columns in which the sulfur dioxide is passed countercurrent to the alkali. The solution is cooled and the sodium metabisulfite is removed by centrifuging or filtration. Rapid drying, eg, in a stream-heated shelf dryer or a flash dryer, avoids excessive decomposition or oxidation to which moist sodium metabisulfite is susceptible.

Shipment and Storage. Sodium metabisulfite can be stored under air at ambient temperatures, but under humid conditions the product cakes and the available SO_2 content decreases as a result of oxidation. Therefore, storage should be under cool, dry conditions. The product is shipped in 22.7- and 45.4-kg polyethylene-lined (moistureproof) bags and 45.4- and 181-kg fiber drums. Steel drums are used for export. The solution is shipped in tank cars and trucks. Dry sodium metabisulfite can be handled in iron or steel equipment. Sodium bisulfite solutions can be handled in 316 and 347 stainless steels, lead, rubber, wood, Haveg, glass-reinforced polyester, or cross-linked polyethylene.

Economic Aspects. U.S. production of sodium metabisulfite is estimated to be well in excess of 45,000 t, but statistics are confused by some commingling with sodium sulfite. The principal U.S. producers are Rhodia and General Chemical. The price in mid-1995 was $0.63/kg for anhydrous sodium bisulfite.

Grades and Specifications. Sodium metabisulfite is available in photographic, food and NF, and technical grades (340). Typical analyses for the food and NF grade are 99 wt% $Na_2S_2O_5$, 0.6 wt% Na_2SO_4; 0.4 wt% Na_2SO_3, 3 ppm iron, 0.2 ppm arsenic, 0.1 ppm lead, and 2 ppm selenium. Typical analyses for the technical grade are 98 wt% $Na_2S_2O_5$, 1.1 wt% Na_2SO_4, 0.8 wt% Na_2SO_3, and 4 ppm iron. An aqueous solution typically assaying 20–42% $NaHSO_3$ is sold in tank trucks.

Health and Safety Factors. Sodium metabisulfite is nonflammable, but when strongly heated it releases sulfur dioxide. The oral acute toxicity is slight and the LD_{50} (rat, oral) is 2 g/kg. Sodium bisulfite appears to be weakly mutagenic to some bacteria, in rodent embryos, and in a human lymphocyte test. There is inadequate evidence for carcinogenicity (234,415).

The solid product and its aqueous solutions are mildly acidic and irritate the skin, eyes, and mucous membranes. The solid material when moist generates the pungent, irritating odor of sulfur dioxide. Food-grade sodium metabisulfite is permitted in those foods that are not recognized as sources of vitamin B_1, with which sulfur dioxide reacts (381) (see VITAMINS, THIAMINE B1).

Uses. Sodium metabisulfite is extensively used as a food preservative and bleach in the same applications as sulfur dioxide. Because sodium metabisulfite is most effective at low pH, the active agent is probably sulfur dioxide or sulfurous acid (412). Sodium bisulfite (sodium metabisulfite) is used in photography (qv), as a reductant, and as a preservative for thiosulfate fixing baths. Other reducing agent applications include reduction of chromate in plating effluents to less toxic chromium salts, which can then precipitate upon addition of lime (416,417). Sodium metabisulfite is also used to reduce chlorine in industrial process water and wastewater. In the textile industry, sodium bisulfite containing metabisulfite is used as a bleach, especially for wool (qv); as an antichlor after bleaching of nylon, for reducing vat dyes; and in rendering certain other dyes soluble. It is a less powerful reductant than sodium dithionite [7775-14-6].

Aqueous sodium bisulfite has been shown to be very effective for removing contaminants, such as sulfur trioxide, dioxide, and hydrogen halides from exhaust gases from coal- or oil-fired burners. The sulfur dioxide can then be removed downstream by a wet scrubber (418). In tanneries, sodium bisulfite is used to accelerate the unhairing action of lime. It is also used as a chemical reagent in the synthesis of surfactants (qv). Addition to alpha-olefins under radical catalyzed conditions yields sodium alkylsulfonates (wetting agents). The addition of sodium bisulfite under base-catalyzed conditions to dialkyl maleates yields the sulfosuccinates.

The reversible addition of sodium bisulfite to carbonyl groups is used in the purification of aldehydes. Sodium bisulfite also is employed in polymer and synthetic fiber manufacture in several ways. In free-radical polymerization of vinyl and diene monomers, sodium bisulfite or metabisulfite are frequently used as the reducing component of a so-called redox initiator (see INITIATORS). Sodium bisulfite is also used as a color preventative and is added as such during the coagulation of crepe rubber.

13.4. Sodium Thiosulfate and Other Thiosulfate Salts. (See THIOSULFATES).

13.5. Sodium Dithionite [7775-14-6]. *Physical Properties.* Sodium dithionite (sodium hydrosulfite, sodium sulfoxylate), $Na_2S_2O_4$, is a colorless solid and is soluble in water to the extent of 22 g/100 g of water at 20°C. It is sold commercially as both the dry solid and as an aqueous solution (such as Olin's Hydrolin).

Chemical Properties. Anhydrous sodium dithionite is combustible and can decompose exothermically if subjected to moisture. Sulfur dioxide is given off violently if the dry salt is heated above 190°C. At room temperature, in the absence of oxygen, alkaline (pH 9–12) aqueous solutions of dithionite decompose slowly over a matter of days. Increased temperature dramatically increases the decomposition rate. A representation of the decomposition chemistry is as follows:

$$2\,S_2O_4^{2-} + H_2O \longrightarrow 2\,HSO_3^{-} + S_2O_3^{2-}$$

The decomposition of dithionite in aqueous solution is accelerated by thiosulfate, polysulfide, and acids. The addition of mineral acid to a dithionite solution produces first a red color that turns yellow on standing; subsequently, sulfur precipitates and evolution of sulfur dioxide takes place (419). Sodium dithionite is stabilized by sodium polyphosphate, sodium carbonate, and sodium salts of organic acids (420).

Sodium dithionite is most stable and effective as a reducing agent in alkaline solutions, although with excess strong alkali the following reaction occurs:

$$3\,Na_2S_2O_4 + 6\,NaOH \longrightarrow 5\,Na_2SO_3 + Na_2S + 3\,H_2O$$

Dithionite is a stronger reducing agent than sulfite. Many metal ions, eg, Cu^{2+}, Ag^{+}, Pb^{2+}, Sb^{3+}, and Bi^{3+} are reduced to the metal, whereas TiO^{2+} is reduced to Ti^{3+} (346). Dithionite readily reduces iodine, peroxides, ferric salts, and oxygen. Some of the decolorizing applications of dithionite, eg, in clay bleaching, are based on the reduction of ferric iron.

Addition of sodium dithionite to formaldehyde yields the sodium salt of hydroxymethanesulfinic acid [79-25-4], $HOCH_2SO_2Na$, which retains the useful reducing character of the sodium dithionite although somewhat attenuated in reactivity. The most important organic chemistry of sodium dithionite involves its use in reducing dyes, eg, anthraquinone vat dyes, sulfur dyes, and indigo, to their soluble leuco forms (see DYES, ANTHRAQUINONE). Dithionite can reduce various chromophores that are not reduced by sulfite. Dithionite can be used for the reduction of aldehydes and ketones to alcohols (421). Quantitative studies have been made of the reduction potential of dithionite as a function of pH and the concentration of other salts (422,423).

Manufacture. A review of older manufacturing processes is available (424). Commercial processes for production of sodium dithionite are based on reduction of sulfite or bisulfite. In order of approximate worldwide production, commercial processes are reduction by sodium formate, zinc, sodium amalgam (425–427), and electrochemical reduction in a membrane cell. The formate process (428–430) was commercialized during the 1970s and has become the predominant manufacturing technology. The zinc process (431) continues to decrease in popularity because of environmental concerns regarding zinc. The amalgam process was commercialized in the late 1960s, but has limited growth because it must be tied to a sodium amalgam source. The electrochemical process, commercialized in the late 1980s, is the newest available technology and utilizes only caustic and sulfur dioxide as raw materials (432). Anhydrous or solution product can be manufactured by all processes; however, the formate and zinc processes typically produce dry product, the amalgam and electrochemical processes typically produce solution product.

Sodium dithionite solution can be produced on-site utilizing a mixed sodium borohydride–sodium hydroxide solution to reduce sodium bisulfite. This process has developed, in part, because of the availability of low cost sulfur dioxide or bisulfite at some paper mills. Improved yields, $> 90\%$ dithionite based on borohydride, can be obtained by the use of a specific mixing sequence and an optimized pH profile (433,434). Electrochemical technology is also being offered for on-site production of sodium hydrosulfite solution (435).

Shipment and Storage. Anhydrous sodium dithionite is shipped in sealed, water-tight containers and must be stored in dry and cool locations. Standard containers are metal drums and semibulk containers. A double inner plastic liner is recommended to prevent access of both water and air. Properly stored dry product can have an effective shelf-life of at least 6–12 months. Dissolving dry product should be accomplished by adding the dry product to the solution to avoid potential ignition of the dry product. In the event of a fire, water in large amounts is recommended. Several designs for automated mixing have been developed to minimize problems with dry dissolving.

The solution product has grown significantly because of health, flammability, storage, and handling issues of the dry product. Dithionite solution can be stored in dedicated, insulated tanks that may be refrigerated for longer term storage. Commercial solution product is stored with an inert atmosphere or vapor barrier.

Economic Aspects. U.S. demand for merchant sodium dithionite (solids basis) was estimated at 104,000 short tons in 2002, projected 110,000 t by 2006. Net imports were 9000 short tons in 2002. There are four North American producers of sodium dithionite. Chemtrade Logistics is the largest producer (45,000-t capacity) with two locations, believed to be mainly using the formate process, Olin (36,000-t capacity), Celanese (30,000-t capacity) and Vulcan (4000-t capacity), in a small solution plant in Wisconsin using the Olin electrochemical process. In addition, it was estimated in 1992 that 13,000 t/year is produced at U.S. pulp mills using the Borol process from sulfur dioxide and sodium borohydride.

Growth is estimated at 2–3%/year. The list price in mid-2003 was ~$0.76/lb (436–438) with substantial discounting for large volume users.

Grades. There are several commercial solid sodium dithionite grades, >90, >88, >85, and ~ 70 wt% dry product (often blended with other stabilizers or additives), and 125-g/L stabilized solution. It is stabilized by ~4 g/L of sodium hydroxide.

Analytical Methods. Various analytical methods involve titration with oxidants, eg, hexacyanoferrate (ferricyanide), which oxidize dithionites to sulfite. Iodimetric titration to sulfate in the presence of formaldehyde enables dithionite to be distinguished from sulfite because aldehyde adducts of sulfite are not oxidized by iodine. Reductive bleaching of dyes can be used to determine dithionite, the extent of reduction being determined photometrically. Methods for determining mixtures of dithionite, sulfite, and thiosulfates have been reviewed (439). Analysis of dithionite particularly for thiosulfate, a frequent and undesirable impurity, can be done easily by liquid chromatography (440).

Health and Safety Factors. Dry sodium dithionite, when exposed to moist air, heats and can ignite spontaneously. In case of fire, the burning material must be deluged with water, as too little water may be worse than none at all. Carbon dioxide and dry extinguishers are ineffective because dithionite provides its own oxygen for combustion. Large amounts of sulfur dioxide are liberated, further complicating fire-fighting efforts. Self-contained breathing units should be worn by all fire fighters.

Sodium dithionite is considered only moderately toxic. The solution is reported to have an LD_{50} (rat, oral) of ~5 g/kg. Another report gives the LD_{50} (rat) as 25 mg/kg (441). It is slightly irritating to skin, but strongly irritating to eyes (rabbit tests). As with sulfites, fairly large doses of sodium dithionite can probably be tolerated because oxidation to sulfate occurs. However, irritation of the stomach and respiratory tract by the liberated sulfurous acid or sulfur dioxide is expected, and as a food additive, sodium dithionite is generally recognized as safe (GRAS) (442).

In 21CFR182.90 sodium dithionite is considered generally recognized as safe (GRAS) for its intended use as a substance that may migrate to food from paper and paperboard products used in food packaging.

Uses. Textile applications have historically been primary uses for dithionite, including dye reduction, dye stripping from fabric, bleaching, and equipment cleaning. These applications have not grown as rapidly and in 2002 consume ~24% of the North American consumption (436). Indigo dyeing of cotton denims has been an important application. Conditions have been discussed for efficient use of sodium hydrosulfite in commercial vat dyeing processes (443).

Pulp and paper bleaching applications have grown and by 2002 represented ~56% of the North American dithionite usage, mainly to brighten mechanical pulps (436). There has also been significant growth in color stripping of secondary fibers and some use in polish bleaching of chemical pulps. The factors controlling bleaching with hydrosulfite have been described (444–446). Hydrogen peroxide competes somewhat. Clay (kaolin) bleaching applications represent ~16% of North American consumption (436). Bleaching by ozone has made some inroads.

Miscellaneous uses include reductive bleaching of glue, gelatin, leather, soap, oils, food products, photographics, and oxygen scavenging in water (used for high pressure boilers or for synthetic rubber polymerization). Because the toxicity of sodium dithionite is only slight, it is permitted in various food-contact applications. Users of dithionites have largely converted from zinc to sodium dithionite, to avoid water pollution problems.

13.6. Zinc Dithionite. Zinc dithionite [7779-86-4], ZnS_2O_4, is a white, water-soluble powder. Although it exhibits somewhat greater stability in aqueous solution compared to sodium dithionite at a given temperature and pH, it is no longer used in the United States because of regulatory constraints on pollution of water by zinc.

13.7. Sodium and Zinc Formaldehyde Sulfoxylates. Although free sulfoxylic acid [20196-46-7], H_2SO_2, has not been isolated and its salts are in doubt, organic derivatives, which may be viewed as adducts of sulfoxylic acid, are commercially made. The latter are mainly sodium formaldehyde sulfoxylate [149-44-0], $HOCH_2SO_2Na$ (commercially sold as the dihydrate) and zinc formaldehyde sulfoxylate [24887-06-7] (424). These compounds are water-soluble reducing agents with uses similar to the dithionites but are more stable. They can be used in reducing and bleaching applications at lower pH values and at somewhat higher temperatures than the dithionites. For example, the formaldehyde sulfoxylates are useful at pH 3.4 as compared to an optimum pH of ~ 6 for zinc dithionite and ~ 9.5 for sodium dithionite. The most stable compound of this series is basic zinc formaldehyde sulfoxylate, which can be used as a reductant at $\sim 100^\circ C$, compared to $\sim 50^\circ C$ for sodium dithionite.

In addition to applications in dyeing, sodium formaldehyde sulfoxylate is used as a component of the redox system in emulsion polymerization of styrene–butadiene rubber recipes.

13.8. Dithionic Acid [14970-71-9] and Metal Dithionates. The dithionate anion is $S_2O_6^{-2}$ and is symmetrical with a $^-O_3S{-}SO_3^-$ structure. Concentrated free dithionic acid [14970-71-9], a strong acid, is unstable. Most of its salts are water soluble. Five dithionate metal salts ($Na_2S_2O_6$ (anhydrous [14970-71-9]; dihydrate [7631-94-9]), CaS_2O_6, BaS_2O_6, MgS_2O_6, $K_2S_2O_6$) are commercially available on a small scale. Note that because of errors in nomenclature, literature references to dithionates often actually pertain to the much more common dithionites. Moreover, dithionic acid is sometimes confused in the literature with pyrosulfuric acid.

Preparation and Analysis. Manganese dithionate was prepared in the nineteenth century via the reaction of MnO_2 with aqueous SO_2. This reaction remains the best known method for producing dithionic acid and its salts (447–449). The major impurities are manganese sulfite and manganese sulfate. The procedure of Carpenter, based on the reaction of ferric oxide and SO_2, does not represent an improved method because sulfite is also produced (450). Preparative metathesis reactions starting with manganese dithionate via membrane-based methodologies represent the best current method for the general manufacture of the other dithionate salts.

One of the unique features of the dithionate anion is its relative instability with respect to hydrolysis–disproportionation at low pH, to form bisulfate and sulfurous acid (451). The analytical method of Soffer permits distinguishing amongst these species (452).

Because of incomplete oxidation of sulfite, liquors from alkaline scrubbing of sulfur dioxide sometimes contain some dithionate. Where it is essential to destroy the dithionate, acidification and heating is effective (453).

Uses. The potential for commercial use of dithionate salts in metal finishing formulations has recently been shown by researchers at Atofina (now Arkema) (454). The good water solubility of the dithionate salts provides an advantage. Plating on steel using copper dithionate plus ammonium dithionate allows higher current density, faster plating, better throwing power, and reduction of cell voltage compared to the conventional plating baths. Nickel plating using dithionate shows better tensile quality and reduction of cell voltage. As a cleaner for removal of rust from steel, ammonium dithionate shows much faster action than ammonium sulfate.

Health and Safety Factors. Very little is known about the specific toxicology of dithionic acid and metal dithionates. The dithionate anion is chemically inert and not expected to be more toxic than comparable neutral sulfur oxide anions, but the specific toxicological properties of the anion are not known.

14. Thiocyanic Acid and its Salts

Free thiocyanic acid [463-56-9], HSCN, can be isolated from its salts, but is not an article of commerce because of its instability, although dilute solutions can be stored briefly. Commercial derivatives of thiocyanic acid are principally ammonium, sodium, and potassium thiocyanates, as well as several organic thiocyanates. The chemistry and biochemistry of thiocyanic acid and its derivatives have been reviewed extensively (455–457).

14.1. Ammonium Thiocyanate. *Physical Properties.* Ammonium thiocyanate [1762-95-4], NH_4SCN, is a hygroscopic crystalline solid that deliquesces at high humidities (375,376). It melts at 149°C with partial isomerization to thiourea. It is soluble in water to the extent of 65 wt% at 25°C and 77 wt% at 60°C. It is also soluble to 35 wt% in methanol and 20 wt% in ethanol at 25°C. It is highly soluble in liquid ammonia and liquid sulfur dioxide, and moderately soluble in acetonitrile.

Chemical Properties. Ammonium thiocyanate rearranges upon heating to an equilibrium mixture with thiourea: 30.3 wt% thiourea at 150°C, 25.3 wt% thiourea at 180°C (456,458). At 190–200°C, dry ammonium thiocyanate decomposes to hydrogen sulfide, ammonia, and carbon disulfide, leaving guanidine thiocyanate [56960-89-5] as a residue. Aqueous solutions of ammonium thiocyanate are weakly acidic; a 5 wt% solution has a pH 4–6.

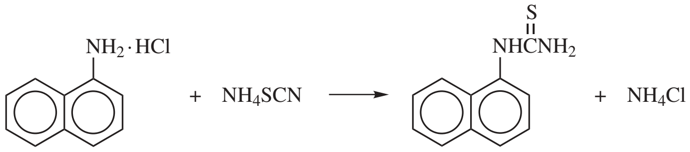
Thiocyanates are rather stable to air, oxidation, and dilute nitric acid. Of considerable practical importance are the reactions of thiocyanate with metal cations. Silver, mercury, lead, and cuprous thiocyanates precipitate. Many metals form complexes. The deep red complex of ferric iron with thiocyanate $[Fe(SCN)_6]^{3-}$, is an effective indicator for either ion. Various metal thiocyanate complexes with transition metals can be extracted into organic solvents.

The organic chemistry of thiocyanates is notably that of nucleophilic displacement of alkyl halides by thiocyanate anion to form alkyl thiocyanates:

$$RCH_2Cl + SCN^- \longrightarrow RCH_2SCN + Cl^-$$

In certain instances, the thiocyanates, eg, allyl thiocyanate [764-49-8] can rearrange to isothiocyanates, eg, allyl isothiocyanate [57-06-7]:

Ammonium thiocyanate reacts with amines yielding thioureas, such as naphthyl thiourea [86-88-4]:



Manufacture. An extensive technology was developed initially in the 1930s for isolation of ammonium thiocyanate from coke-oven gases, but this technology is no longer practiced in the United States (455). However, such thiocyanate recovery processes are used industrially in Europe. Likewise, the direct sulfurization of cyanides to thiocyanates is not practiced commercially in the United States. The principal route used in the United States is the reaction of carbon disulfide with aqueous ammonia, which proceeds by way of ammonium dithiocarbamate [513-74-6]. Upon heating, the ammonium dithiocarbamate decomposes to ammonium thiocyanate and hydrogen sulfide.

$$CS_2 + 2\,NH_3\,(aq) \longrightarrow NH_2\overset{\overset{S}{\|}}{C}SNH_4 \longrightarrow NH_4SCN + H_2S$$

In a typical batch operation, carbon disulfide is added to four molar equivalents of 25–30 wt% aqueous ammonia in a stirred vessel, which is kept closed for the first one to two hours. The reaction is moderately exothermic and requires cooling. After 2–3 h, when substantially all of the disulfide has reacted, the reaction mixture is heated to decompose dithiocarbamate and trithiocarbonate and vented to an absorption system to collect ammonia, hydrogen sulfide, and any unreacted carbon disulfide.

This reaction can also be run in a continuous fashion. In the initial reactor, agitation is needed until the carbon disulfide liquid phase reacts fully. The solution can then be vented to a tower where ammonia and hydrogen sulfide are stripped countercurrently by a flow of steam from boiling ammonium thiocyanate solution. Ammonium sulfide solution is made as a by-product. The stripped ammonium thiocyanate solution is normally boiled to a strength of 55–60 wt%, and much of it is sold at this concentration. The balance is concentrated and cooled to produce crystals, which are removed by centrifugation.

Shipment and Storage. The crystalline material is shipped as a nonhazardous material, in polyethylene-lined fiber drums. The solution can be shipped in drums or bulk. Suitable materials of construction for handling ammonium thiocyanate are aluminum, 316 stainless steel, rubber, poly(vinyl chloride), and glass-reinforced epoxy. Steel, 304 stainless steel, and copper alloys should be avoided (458,459).

Economic Aspects. Ammonium thiocyanate capacity in the United States is well in excess of 9000 t/year on a 100% solids basis, but production in the 1990s is substantially less than this capacity. In the United States only Witco produces ammonium thiocyanate. Production growth is small. The price of ammonium thiocyanate in mid-1995 was $2.02/kg.

Grades and Specifications. A technical crystal of 98% minimum assay with ~2 wt% maximum water content is commercially available, as well as a 50–55 wt% aqueous solution (458,459). The latter is the predominant product.

Analytical Methods. Thiocyanate is quantitatively precipitated as silver thiocyanate, and thus can be conveniently titrated with silver nitrate. In the presence of a ferric salt, a red-brown color, produced by the ferric thiocyanate compex, indicates the end point.

Health and Safety Factors. The lowest published human oral toxic dose is 430 mg/kg, causing nervous system disturbances and gastrointestinal symptoms. The LD_{50} (rat, oral) is 750 mg/kg (234). Thiocyanates are destroyed readily by soil bacteria and by biological treatment systems in which the organisms become acclimatized to thiocyanate. Pyrolysis products and combustion products can include toxic hydrogen cyanide, hydrogen sulfide, sulfur oxides, and nitrogen oxides.

Uses. Ammonium thiocyanate is a chemical intermediate for the synthesis of several proprietary agricultural chemicals, mainly herbicides. Its use as a nonselective herbicide is obsolete, although it is still employed as an adjuvant for aminotriazole in nonselective herbicides, which are used principally for brush and perennial weed control. It also is used in photography as a stabilizing agent. It makes undeveloped silver halide substantially insensitive to light. An old use that is practiced is the incorporation of ~0.1 wt% ammonium thiocyanate in ammoniacal nitrogen fertilizer solutions to inhibit the corrosion of steel. It is also used in various rustproofing compositions. Ammonium thiocyanate was used in the separation of hafnium from zirconium; hafnium is extracted as a thiocyanate complex into an organic phase. This use has declined with the nuclear industry in the United States.

There are many smaller specialized uses for ammonium thiocyanate, including stabilization of glue formulations, as an ingredient in antibiotic fermentations, and as an adjuvant in textile dyeing and printing. A rapidly developing newer use is as a tracer in oil fields. The flow pattern of injected water in enhanced oil recovery operations can be followed by taking water samples from producing wells and analyzing them for thiocyanate by colorimetric measurement of the red ferric complex.

14.2. Sodium and Potassium Thiocyanates.

Physical and Chemical Properties. Sodium thiocyanate [540-72-7], NaSCN, is a colorless deliquescent crystalline solid (mp 323°C). It is soluble in water to the extent of 58 wt% NaSCN at 25°C and 69 wt% at 100°C. It is also highly soluble in methanol and ethanol, and moderately soluble in acetone. Potassium thiocyanate [333-20-0], KSCN, is also a colorless crystalline solid (mp 172°C) and is soluble in water to the extent of 217 g/100 g of water at 20°C and in acetone and alcohols. Much of the chemistry of sodium and potassium thiocyanates is that of the thiocyanate anion (455–457).

Manufacture, Shipment, and Analysis. In the United States, sodium and potassium thiocyanates are made by adding caustic soda or potash to ammonium thiocyanate, followed by evaporation of the ammonia and water. The products are sold either as 50–55 wt% aqueous solutions, in the case of sodium thiocyanate, or as the crystalline solids with one grade containing 5 wt% water and a higher assay grade containing a maximum of 2 wt% water. In Europe, the thiocyanates may be made by direct sulfurization of the corresponding cyanide. The acute LD_{50} (rat, oral) of sodium thiocyanate is 764 mg/kg, accompanied by convulsions and respiratory failure; LD_{50} (mouse, oral) is 362 mg/kg. The lowest published toxic dose for potassium thiocyanate is 80–428 mg/kg, with hallucinations, convulsions, or muscular weakness. The acute LD_{50} (rat, oral) for potassium thiocyanate is 854 mg/kg, with convulsions and respiratory failure.

Shipping, analysis, and safety factors are similar to those of ammonium thiocyanate, except that the alkali thiocyanates are more thermally stable. Sodium thiocyanate is best handled in 316 stainless steel. At room temperature, where some iron contamination can be tolerated, type 304 can be used. Aluminum corrodes more rapidly than stainless steel, but some alloys can be used $< 60°C$. Some but not all rubber equipment is satisfactory.

Economic Aspects. Capacity for sodium thiocyanate in the United States is substantially the same as that for ammonium thiocyanate because both products can be made in the same plants, but production is estimated at only slightly > 1000 t. The rate of growth is slight. The price on a 100 wt% basis in 1995 was $2.10/kg. Most sodium thiocyanate is sold as the solution. Potassium thiocyanate is a much lower volume product.

Uses. The largest use for sodium thiocyanate is as the 50–60 wt% aqueous solution, as a component of the spinning solvent for acrylic fibers (see Fibers, acrylic; Acrylonitrile polymers). Other textile applications are as a fiber swelling agent and as a dyeing and printing assist. A newer commercial use for sodium thiocyanate is as an additive to cement in order to impart early strength to concrete (459).

Sodium thiocyanate and other thiocyanate salts are used to prepare organic thiocyanates, eg, methylene dithiocyanate [6317-18-6], Verichem's N-948, a broad-spectrum industrial biocide used as a slimicide in paper production, also for controlling microbial growth in cooling water, cutting oils and fluids, hides, oil-field injection waters, drilling muds, adhesives, paints, and other polymer emulsions.

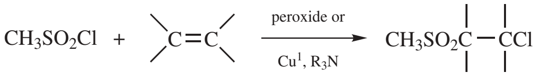
Lesser amounts of sodium thiocyanate are used in color-toning photographic paper, as a stabilizer in rapid film development, and as a sensitizing agent in color negative-film emulsions. It is also used as a brightener in copper electroplating.

15. Methanesulfonic Acid and its Derivatives

15.1. Methanesulfonyl Chloride. *Physical Properties.* Methanesulfonyl chloride [124-63-0] (MSC), CH_3SO_2Cl, is a clear liquid, and is soluble in a wide variety of organic solvents, eg, methanol and acetone (Table 9).

Chemical Properties. Methanesulfonyl chloride is a reactive chemical that allows introduction of the mesyl group, $CH_3SO^-{}_2$, into a wide range of substrates. MSC undergoes free-radical-initiated addition to olefins to produce chloro-substituted sulfones (460–462) (eq. 1). With strong bases, MSC can undergo dehydrochlorination to a transitory reactive intermediate, $CH_2{=}SO_2$, which can dimerize or undergo various addition reactions (463–465). MSC undergoes reactions with alcohols, amines, active methylene compounds (in the presence of bases), and aromatic hydrocarbons (in the presence of Friedel-Crafts catalysts) to replace, generally, a hydrogen atom by a methanesulfonyl group (466–484).

The $CH_3SO_2{-}O{-}$ group in methanesulfonate esters is a good leaving group, facilitating nucleophilic displacements. The utility of MSC for methanesulfonylation is well known in the agricultural, pharmaceutical, and specialty chemical industries. Methanesulfonyl chloride is a product of Elf Atochem North America (469–471).



$$CH_3SO_2Cl + {>}C{=}C{<} \xrightarrow[\text{Cu}^{\text{I}},\ R_3N]{\text{peroxide or}} CH_3SO_2C{-}CCl \qquad (1)$$

Manufacture. Methanesulfonyl chloride is made commercially either by the chlorination of methyl mercaptan or by the sulfochlorination of methane. The product is available in 99.5% assay purity by Elf Atochem NA (now Arkema) in the United States or by Elf Atochem SA in Europe.

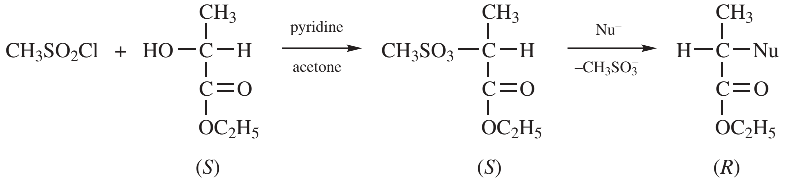
Shipment and Storage. The weight per gallon is 5.6 kg. MSC is shipped and stored in 55-gal (0.208 m^3) steel drums or 5-gal (0.02 m^3) steel pails with a polyethylene liner. Anhydrous MSC is also corrosive toward titanium, titanium−palladium, and zirconium as measured in metal strip tests at 50°C. It is classified as a corrosive liquid.

Health and Safety Factors. MSC has a vapor toxicity on mice of LD_{50} 4.7 mg/L. It is a lachrymator and in order to prevent contact with eyes, goggles should be worn. It is also corrosive to skin and therefore chemically resistant gloves and protective clothing should be worn to prevent contact with skin. Containers should only be opened where there is adequate ventilation.

Uses. Most applications of MSC are for intermediates in the pharmaceutical, photographic, fiber, dye, and agricultural industries. There also are miscellaneous uses as a stabilizer, catalyst, curing agent, and chlorination agent.

Some important applications of MSC are shown in equations 2–4 (471,483). A pharmaceutical intermediate, 2-azabicyclo[2.2.1]hept-5-en-3-one is produced by equations 3 and 4.

MSC for asymmetric synthesis

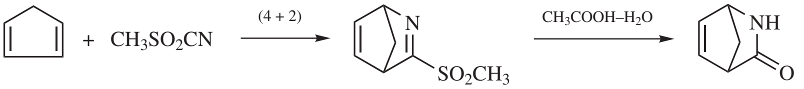


$$CH_3SO_2Cl + HO-\overset{CH_3}{\underset{C(=O)OC_2H_5}{C}}-H \xrightarrow[\text{acetone}]{\text{pyridine}} CH_3SO_3-\overset{CH_3}{\underset{C(=O)OC_2H_5}{C}}-H \xrightarrow[-CH_3SO_3^-]{Nu^-} H-\overset{CH_3}{\underset{C(=O)OC_2H_5}{C}}-Nu \quad (2)$$

(*S*) (*S*) (*R*)

Methanesulfonyl cyanide as a dienophile

$$CH_3SO_2Cl \xrightarrow{Na_2SO_3-NaHCO_3} CH_3SO_2Na \xrightarrow{ClCN} CH_3SO_2CN \quad (3)$$



(4)

15.2. Methanesulfonic Acid. *Physical Properties.* Methanesulfonic acid [75-75-2] (MSA), CH_3SO_3H, is a clear, colorless, strong organic acid available in bulk quantities from Elf Atochem North America as a 70% solution and on an anhydrous basis (100%). MSA is soluble in water and in many organic solvents. Its physical properties are described in Table 10.

Chemical Properties; Uses. Methanesulfonic acid combines high acid strength with low molecular weight. Its pK_a (laser Raman spectroscopy) is -1.9, about twice the acid strength of HCl and half the strength of sulfuric acid. MSA finds use as catalyst for esterification, alkylation, and in the polymerization and curing of coatings (485,487,488). The anhydrous acid is also useful as a solvent.

The metal salts of MSA are highly soluble in water as well as in some organic solvents, making MSA useful in electroplating operations. For example, lead sulfate is insoluble in water, whereas lead methanesulfonate (lead mesylate) is water soluble.

Methanesulfonic acid also finds use in preparing biological and agricultural chemicals, textile treatment chemicals, and for plastics and polymers. Various high molecular weight polymers are soluble in MSA, it is biodegradable and can be recycled, it has an advantage in many applications in that it is a nonoxidizing acid which results in no charring and minimal byproducts, and because of this it is a preferred acid for catalyzing esterifications to give low color ester products.

Specifically MSA has been found to be more effective than *p*-toluenesulfonic acid and sulfuric acid in preparing dioctyl phthalate (488). A U.S. patent also discloses its use to prepare light-colored fatty esters (489). It is also important as a catalyst to prepare acrylates, methacrylates, adipates, phthalates, trimellitates, thioglycolates, and other esters.

The use of MSA as catalyst to prepare 2-alkylphenols and 2,6-dialkylphenols has been described (490).

Methanesulfonic acid and other lower alkanesulfonic acids are useful for plating of lead, nickel, cadmium, silver, and zinc (491,492). It also finds use in plating of tin, copper, lead, and other metals and is used in printed circuit board manufacture. In metal finishing the metal coating can be stripped chemically or electrolytically with MSA. It also finds use in polymers, as a polymer solvent and as a catalyst for polymerization of monomers such as acrylonitrile. Methanesulfonic acid finds use in ion-exchange resin regeneration because of the high solubility of many metal salts in aqueous solutions.

The popularity of MSA as an electrolyte in electrochemical applications has developed as a result of the following unique physical and chemical properties: (*1*) exhibits low corrosivity and is easy to handle, (*2*) nonoxidizing, (*3*) manufacturing process yields a high purity acid, (*4*) exceptional electrical conductivity, (*5*) high solubility of metal salts permits broad applications, (*6*) MSA-based formulations are simpler, (*7*) biodegradable, and (*8*) highly stable to heat and electrical current.

Health and Safety Factors. Methanesulfonic acid is a strong toxic acid and is corrosive to skin. The acute oral toxicity of the sodium salt in mice LD_{50} is 6.2 g/kg. The 1976 edition of the NIOSH Registry of Toxic Effects of Chemical Substances lists certain reaction products of MSA as having suspected mutagenic, teratogenic, and carcinogenic activity (493).

Manufacture. Methanesulfonic acid is made commercially by oxidation of methyl mercaptan by chlorine in aqueous hydrochloric acid to give methanesulfonyl chloride that is then hydrolyzed to MSA.

Shipping and Storage. Methanesulfonic acid is shipped in tank trucks and in plastic 55-gal drums or smaller containers with polyethylene inserts. The freight classification is Alkyl Sulfonic Acid, Liquid; 8 Corrosive Material, UN 2586, Chemical N01BN.

15.3. Methanesulfonamide and *N*-Alkyl Methanesulfonamides.

Physical Properties. Methanesulfonamide [3144-09-0] is available commercially in the United States and China. The product from Arkema Group, Inc. has been sold under the name of MSAM in a pure crystalline form, mp 89.5–91°C (494,495). It is low in volatility, having a vapor pressure of 3 mm at 105°C and 20 mm at 180°C. It is very soluble in water, to ~50% by weight at 25°C, and moderately soluble in isopropyl alcohol.

N-Methylmethanesulfonamide (494) has been available from Arkema as a water-miscible liquid, bp 117–118°C at 0.3 mm, refractive index 1.4508 at 23°C, density 1.277 g/cm^3 at 30°C.

Chemical Properties. Methanesulfonamides are quite stable hydrolytically, but the *N*-hydrogens are more acidic than those of a carboxamide, and are removable by moderately strong bases. The resultant anion can be readily alkylated or arylated. Other chemistry of methanesulfonamide, mostly substitution on the nitrogen, has been described, using alkyl halides, acyl halides, epoxides, aldehydes, isocyanates, cyanates, carbon disulfide and thionyl chloride (494–498).

Manufacture. Methanesulfonamide is produced commercially by the reaction of methanesulfonyl chloride and ammonia by a patented process (499–501). *N*-Methylmethanesulfonamide is produced analogously using methylamine.

Uses. Methanesulfonamide is reacted with a substituted benzoyl chloride, to produce 5-[2-chloro-4-(trifluoromethyl)phenoxy]-*N*-(methylsulfonyl)-2-nitrobenzamide (fomesafen) [72178-02-0], a herbicide used for postemergence weed control in soybeans (502).

N-Methyl methanesulfonamide is a pharmaceutical intermediate.

Health and Safety Factors. Information from the manufacturer indicates that methanesulfonamide is of very low toxicity, with LD_{50} (rat, oral) > 4000 mg/kg. Although skin contact should be minimized, it has only slight dermal toxicity.

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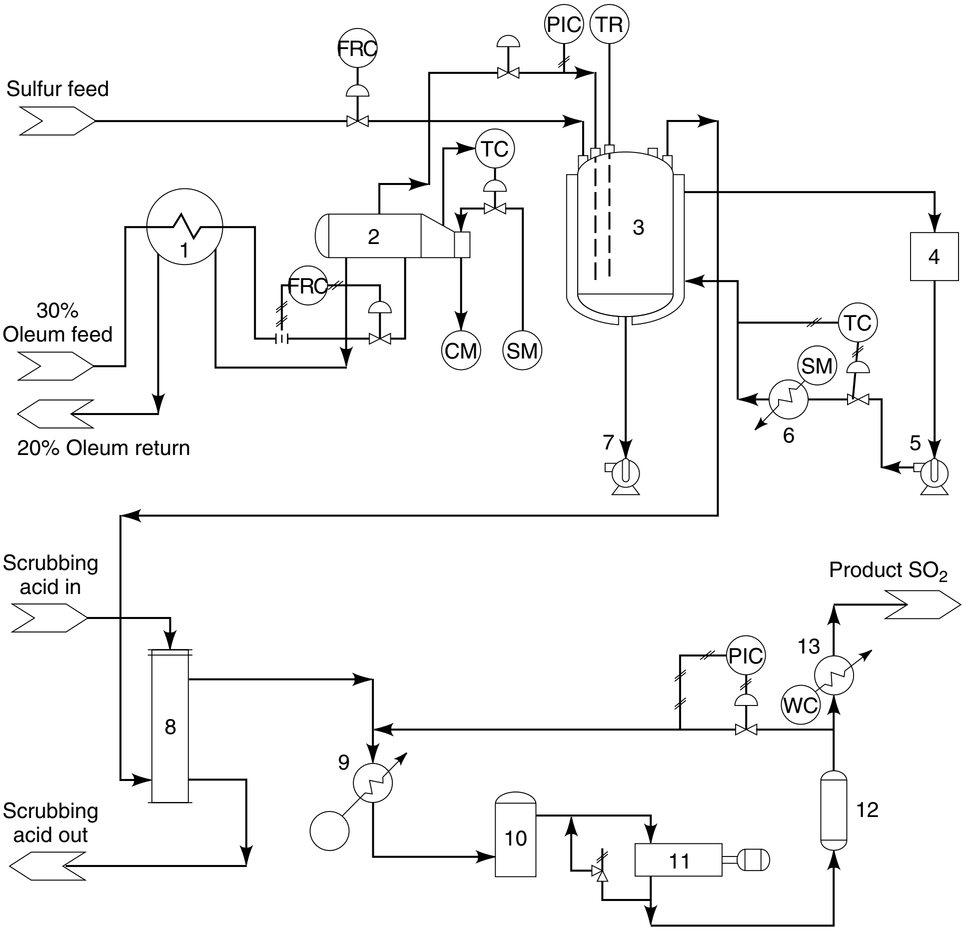

Fig. 1. Flow diagram of production of sulfur dioxide from oleum: (*1*) 30% oleum exchanger; (*2*) SO_3 vaporizer; (*3*) reactor; (*4*) coolant surge tank; (*5*) coolant circulating pump; (*6*) coolant exchangers; (*7*) sludge and acid pump; (*8*) scrubber; (*9*) SO_2 cooler; (*10*) gas cleaner; (*11*) SO_2 compressor; (*12*) pulsation damper; and (*13*) SO_2 condenser. CM is the condensate; FRC, flow recording controller; PIC, pressure indicating controller; SM, steam; TC, temperature recorder; and WC, cooling water (325).

Table 1. **Physical and Thermodynamic Properties of Carbonyl Sulfide**

Property	Value	References
mol wt	60.074	14
mp, °C	−138.8	15
bp, °C	−50.2	15
ΔH fusion, at 134.3 K, kJ/mol[a]	4.727	15
ΔH vaporization, at 222.87 K, kJ/mol[a]	18.57	15
density at 220 K, 101.3 kPa(= 1 atm), g/cm^3	1.19	15
sp gr, gas at 298 K (air = 1)	2.10	15
critical temperature, °C	105	15
critical pressure, kPa[b]	5946	15
critical volume, cm^3/mol	138	15
triple point, K	134.3	15
ΔG formation, at 25°C, kJ/mol[a]	−169.3	2
ΔH formation, at 25°C, kJ/mol[a]	−142.1	2
S formation, at 25°C, J/(mol·K)[a]	231.5	2
C_p, at 25°C, J/(mol·K)[a]	41.5	2
autoignition temperature in air, °C	~250	15
flammability limits in H_2O-saturated air at 17.9°C, vol%		
upper limit	9.6	
lower limit	33.2	15
solubility in water at 101.3 kPa(= 1 atm), vol%		
0°C	0.356	15
10°C	0.224	
20°C	0.149	

[a] To convert J to cal, divide by 4.184.

[b] To convert kPa to psi, multiply by 0.145.

Table 2. **Physical and Thermodynamic Properties of Hydrogen Sulfide**

Property	Value	References
mol wt	34.08	98
mp, °C	−85.53	99
bp, °C	−60.31	99
ΔH fusion, kJ/mol[a]	2.375	98
ΔH vaporization, kJ/mol[a]	18.67	98
density at −60.31°C, kg/m^3	949.6	99
sp gr, gas (air = 1)	1.182[b]	101
critical temperature, °C	100.38	102
critical pressure, kPa[c]	9006	102
critical density, kg/m^3	346.0	102
ΔG formation, kJ/mol[a]	−33.6	14
ΔH formation, at 25°C, kJ/mol[a]	−20.6	14
S formation, at 25°C, J/(mol·K)[a]	205.7	14
C_p, at 27°C, J/(mol·K)[a]	34.2	14
autoignition temperature in air, °C	~ 260	103
explosive range in air at 20°C, vol%		
upper limit	46	103
lower limit	4.3	
vapor pressure, kPa[c]		
−60°C	102.9	99,104
−40°C	257.9	99
−20°C	562.0	99
0°C	1049	99
20°C	1814	99
40°C	2937	99
60°C	4480	99
solubility in water,[d] g/100 g soln		101
0°C	0.710	
10°C	0.530	
20°C	0.398	

[a] To convert J to cal, divide by 4.184.

[b] Based on air = 79 mol % nitrogen plus 21 mol % oxygen.

[c] To convert kPa to psi, multiply by 0.145; to convert kPa to bars, divide by 100.

[d] At 101.3 kPa(= 1atm) total pressure.

Table 3. **Oxidation Reactions of Hydrogen Sulfide**

Oxidizing agent	Conditions	Sulfur-containing products
O_2	flame	SO_2, some SO_3
	flame or furnace, catalyst (Claus process)	sulfur
	aqueous soln of H_2S, catalyst	sulfur
H_2O_2	neutral; alkaline solution	sulfur; SO_3^{-2}, SO_4^{-2}
Na_2O_2	dry, elevated temperature	Na_2S, Na_2S_x
O_3	aqueous	sulfur, H_2SO_4
SO_2	elevated temperature, catalyst	sulfur
	aqueous soln	sulfur, polythionic acids
H_2SO_4	concentrated acid	sulfur, SO_2
HNO_3	aqueous	H_2SO_4
NO	silica gel catalyst	sulfur
NO_2^-	aqueous at pH 5–7	sulfur, NO
	aqueous at pH 8–9	sulfur, NH_3
Cl_2	gaseous, excess Cl_2	SCl_2
	gaseous, excess H_2S	sulfur
	aqueous soln, excess Cl_2	H_2SO_4
I_2	aqueous soln	sulfur (quantitative)
Fe^{3+}	aqueous soln	sulfur, FeS

Table 4. **Effects of Hydrogen Sulfide Inhalation on Humans**[a]

Number of people exposed	Concentration, mg/m^3	Duration of exposure	Effect
1	17,000		death
1	2800–5600	<20 min	death
10	1400	<1 min	unconsciousness, abnormal (electrocardiogram) ECG; death of one person
342	1400–2800	<20 min	hospitalization of 320, death of 22 including 13 in hospital, residual nervous system damage in 4
5	1400	instant	unconsciousness, death
1	1400	<25 min	unconsciousness, low blood pressure, pulmonary edema, convulsions, hematuria
4	400–760		unconsciousness
1	320	20 min	unconsciousness, arm cramps, low blood pressure
78	20–35		burning eyes in 25, headache in 32, loss of appetite in 31, weight loss in 20, dizziness in >19
6500	15–20	4–7 h	conjunctivitis
population of Terre Haute, Indiana	0.003–11	intermittent air pollution episodes over a 2-month period	nausea in 13, headache, shortness of breath in 4, sleep disturbance in 5, throat and eye irritation in 5

[a] Ref. 160.

Table 5. **Physical and Thermodynamic Properties of Sulfur Monochloride, S_2Cl_2**

Property	Value	References
mol wt	135.03	180,181
mp, °C		
commercial	−76	180,181
pure	−76.1	180,181
bp, °C	137.8	180,181
specific gravity, 20°C	1.68	180,181
refractive index, $n^{20}{}_D$	1.670	180,181
flash point, Cleveland open cup, °C	130	180,181
vapor pressure, kPa[a]		180,181
0°C	0.479	180,181
21.1°C	1.513	180,181
37.7°C	3.5	180,181
solubility in water	insoluble	180,181
ΔH formation, at 25°C, kJ/mol[b]		
liquid	−32	182, 183
gas	−58	182, 183
molar heat capacity, J/(mol·K),[b] °C	115	184
specific heat at 25°C, J/g[b]	0.92	184
heat of hydrolysis, J/mol[b]	146.44	184
heat of vaporization, J/mol[b]	36,401	184

[a] To convert kPa to mmHg, multiply by 7.5.

[b] To convert J to cal, divide by 4.184.

Table 6. **Physical and Thermodynamic Properties of Thionyl Chloride**

Property	Value	References
mol wt	118.98	218
mp, °C	−104.5	218
bp, °C	76	218
specific gravity, 25°C	1.63	218
molar heat capacity, J/(mol·K)[a]	120.5	218
latent heat of vaporization, kJ/mol[a]	31.0	218
viscosity, mPa·s(= cP)		
0°C	0.81	218
25°C	0.60	218
refractive index, $n^{20}{}_D$	1.517	218
electrical conductivity at 25°C, S/cm(= mho/cm)	2×10^{-6}	218
vapor pressure, kPa[b]		
−20°C	1.5	219
0°C	4.5	
5°C	5.9	
20°C	11.6	
26°C	14.7	
ΔH formation at 25°C, kJ/mol[a]		
liquid	−246	14
gas	−213	14
ΔG formation gas, at 25°C, kJ/mol[a]	−198	14
S formation, J/(mol·K)[a]	309	14
C_p, at 25°C J/(mol·K)[a]		
liquid	121	14
gas	66.5	14

[a] To convert J to cal, divide by 4.184.

[b] To convert kPa to mmHg, multiply by 7.5.

Table 7. **Physical and Thermodynamic Properties of Sulfuryl Chloride**

Property	Value	References
mol wt	134.968	14
mp, last crystal point, °C	−54	248
bp, °C	69.1	248
density, at 25°C, g/cm^3	1.6570	249
latent heat of vaporization, kJ/mol[a]	27.95	248
surface tension at 23.5°C, mN/m(=dyn/cm)	35.26	249
viscosity, mPa·s(=cP)		
0°C	0.918	248
37.8°C	0.595	248
refractive index, $n^{20}{}_{\mathrm{D}}$	1.443	248
vapor pressure, kPa[b]		
0°C	5.45	248
18°C	12.69	
68.7°C	99.3	
coefficient of expansion, 0−38°C, °C-1	0.0012	248
electrical conductivity, S/cm	3×10^{-8}	248
ΔH formation, at 25°C, kJ/mol[a]		
liquid	−394	14
gas	−364	14
ΔG formation gas, at 25°C, kJ/mol[a]	−320	14
S gas, at 25°C, J/(mol·K)[a]	311	14
C_p, at 25°C, J/(mol·K)[a]		
liquid	134	14
gas	77	14

[a] To convert J to cal, divide by 4.184.

[b] To convert kPa to mmHg, multiply by 7.5.

Table 8. **Physical and Thermodynamic Properties of Sulfur Dioxide**

Property	Value	References
mol wt	64.06	14
mp, °C	−72.7	272
bp, °C	−10.02	269
ΔH fusion, kJ/mol[a]	7.40	269
ΔH vaporization, at −10.0°C, kJ/mol[a]	24.92	269
vapor density, at 0°C, 101.3 kPa(=1 atm), air = 1	2.263	269
liquid density, at −20°C, g/cm^3	1.50	272
critical temperature, °C	157.6	272
critical pressure, kPa[b]	7911	272
critical volume, cm^3/g	122.0	272
ΔG formation gas, at 25°C, kJ/mol[a]	−300.19	14
ΔH formation gas, at 25°C, kJ/mol[a]	−296.82	14
S formation gas, at 25°C, J/(mol·K)[a]	248.1	14
C_p gas, at 25°C, J/(mol·K)[a]	39.9	14
dielectric constant at −16.5°C	17.27	269
dipole moment at 25°C, C·m[c]	3.87×10^{-30}	
vapor pressure, kPa[b]		
10°C	230	273
20°C	330	
30°C	462	
40°C	630	
solubility in water, at 101.3 kPa, g/100 g H_2O		274
0°C	22.971	
10°C	16.413	
20°C	11.577	
30°C	8.247	
40°C	5.881	

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[a] To convert J to cal, divide by 4.184.

[b] To convert kPa to psi, multiply by 0.145.

[c] To convert C·m to D, divide by 3.336×10^{-30}.

Table 9. **Physical Properties of MSC**

Property	Value
mol wt	114.6
bp, at 97.3 kPa (730 mmHg), °C	161
refractive index, at 25°C, $n^{20}{}_{\mathrm{D}}$	1.45
freezing point, °C	−33
viscosity, at 25°C, $\mathrm{mm^2/s}$ (=cSt)	1.33
specific gravity	
20°C	1.475
30°C	1.467
flash point, COC,[a] °C	>230
coefficient of cubical expansion, °C-1	0.00082
solubility in water	insoluble (hydrolyzes)
latent heat of vaporization,[b] kJ/kg[c]	349

[a] Cleveland open cup.

[b] Calculated value at the boiling point.

[c] To convert kJ/kg to Btu/lb, multiply by 0.4303.

Table 10. **Physical Properties of MSA**[a]

Property	Value	
	70%	99.5%[b]
formula weight		96.1
MSA content, %	69.5−70.5	99.5[b]
appearance	clear	clear
color, APHA	200	150
freezing point, °C	−60	+19
boiling point,[c] °C		122
refractive index, at 25°C		1.4308
density, at 25°C, $\mathrm{g/cm^3}$		1.47−1.483

[a] Refs. 485 and 486.

[b] Value is minimum.

[c] At 0.133 kPa (1.0 mmHg).