FLUORINE-CONTAINING COMPOUNDS OF SULFUR

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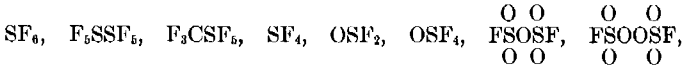
I. Introduction

In the years since World War II a remarkable growth has occurred in the knowledge of compounds of sulfur which contain fluorine. The number of known compounds of this type has increased several fold and the information about some substances known for many years, particularly sulfur hexafluoride, has expanded greatly. The reason for this growth is to be found largely in the awakened interest in fluorine chemistry initiated by the atomic energy program. A part of the effort devoted to fluorine chemistry in the universities, industrial laboratories, and government laboratories in the United States, England, Germany, and, to a lesser degree, Russia, has been spent on compounds of sulfur. The laboratory which has been the most productive of published results is that of Cambridge University.

A second factor which is responsible for the discovery of many new compounds is the electrochemical technique of Simons (*281, 282*) for the synthesis of fluorides by the electrolysis of hydrogen fluoride containing various solutes. By this method many sulfonyl fluorides and perfluoroalkane sulfonic acids have been prepared for the first time.

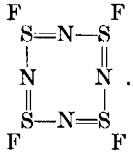
Still a third stimulus is the potential usefulness in industry of some of the compounds. This factor has been particularly important in research on sulfur hexafluoride, fluorosulfonic acid, and the perfluoroalkanesulfonic acids.

The large number of fluorine-containing compounds of sulfur results from the ability of sulfur to form strong covalent bonds with itself or with fluorine, oxygen, carbon, chlorine, phosphorus, and nitrogen. It is also important that sulfur may have coordination numbers of 2, 3, 4, 5, and 6. Formulas of a few compounds which illustrate the versatility of sulfur are:



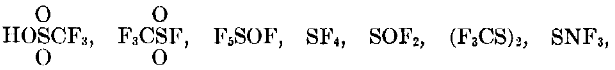
SF_6, F_5SSF_5, F_3CSF_5, SF_4, OSF_2, OSF_4, $F\overset{O}{\underset{O}{S}}O\overset{O}{\underset{O}{S}}F$, $F\overset{O}{\underset{O}{S}}OO\overset{O}{\underset{O}{S}}F$,

$HO\overset{O}{\underset{O}{S}}F$, $F\overset{O}{\underset{O}{S}}F$, $HO\overset{O}{\underset{O}{S}}CF_3$, $F_3CSSSCF_3$, F_3CSCl, SPF_3, ClO_2SO_3F,



Most of the recent syntheses of new compounds have to do with: (1) substances containing $-CF_3$ or other fluorocarbon radicals, (2) substances containing $-SF_5$ radicals, (3) oxyfluorides or salts containing oxyfluoride anions, (4) compounds of S, N, and F.

It may be expected that new compounds will continue to come to light. Research in applied chemistry should find use both for the new and the older compounds. Some of the substances should, for example, prove to be valuable reagents. This applies particularly to very reactive compounds such as



$HO\overset{O}{\underset{O}{S}}CF_3$, $F_3C\overset{O}{\underset{O}{S}}F$, F_5SOF, SF_4, SOF_2, $(F_3CS)_2$, SNF_3,

and others.

As chemists become increasingly aware of these compounds more and more studies shall probably be made. The opportunities for studies by physical chemists are particularly great. For example, almost no studies of kinetics of reactions involving these fluorides have been made.

This review covers nearly the complete literature on fluorine-containing compounds of sulfur up through 1956. That is the last year for which a subject index for Chemical Abstracts or Chemisches Zentralblatt was available. Articles appearing through 1958 are also included when known to the reviewer. In the case of carbon compounds the review deals with the first member of an homologous series, for example

$$\mathrm{HO}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{S}}}\mathrm{CF_3}$$

but does not go into detail about other members of the series. No attempt has been made to cover double salts such as $Al_2(SO_4)_3 \cdot 4AlF_3 \cdot 12H_2O$, $K_3HS_2O_7F_2 \cdot H_2O$, etc. These have been reviewed previously (*211*).

Other reviews of a part of the material covered in this article are to be found in the literature (*2, 37, 178a, 211, 253, 272, 306*).

The earliest reference used in this review is dated 1888. In it and in the larger paper which followed in 1889 Thorpe and Rodgers (*299*) reported the preparation and properties of SPF_3. With the exception of its length, a paper of this quality would be readily accepted for publication today. This was a good beginning for fluorine-containing compounds of sulfur.

II. Fluorides of Sulfur

A. SULFUR HEXAFLUORIDE

Sulfur hexafluoride was first produced by Moissan (*215*) in 1891 and prepared and studied by Moissan and Lebeau (*216*) in 1900 using the combustion of sulfur in fluorine as the preparative method. Although sulfur hexafluoride may be obtained in other ways, including the combustion in fluorine of compounds of sulfur (*225, 227, 228*) and the electrolysis of solutions of sulfides, for example hydrogen sulfide in liquid hydrogen fluoride (*244, 280*), the original method of preparation is still preferred (*100, 101, 190, 211, 241, 269, 330*) and is now used industrially (*100, 101*). To obtain pure sulfur hexafluoride the crude gas may be scrubbed with a solution of KOH or NaOH to remove HF and lower fluorides of sulfur. The gas is then heated to about 300°–400° to convert S_2F_{10} to SF_6 and SF_4. The latter may be removed by a second treatment with base (*100, 190, 269, 270*). In a typical case a sample of the combustion products of sulfur was found to contain 94.3% ($SF_6 + S_2F_{10}$), 1.9% ($SF_4 + S_2F_2$), 2.4% SO_2, 0.4% HF,

TABLE I

PROPERTIES OF SULFUR HEXAFLUORIDE

		Reference	Other references
Vapor pressure			
Solid (−72° to −51°): $\log_{10} P_{mm} = 8.7648 - 1231.3/T$		*331*	*143, 168, 226, 228, 271*
Liquid (−50° to 40°): $\log_{10} P_{mm} = 7.308 - 907.98/T$		*212*	*271*
Transition temperature (°K)	94.3	*92*	
Sublimation temperature 760 mm, (°C)	−63.8	*168*	
Melting point (°C)	−50.8°	*168*	
Critical temperature (°C)	45.642, 45.547	*318, 204*	*4, 212, 242*
Critical pressure (atm)	37.193, 37.113, 36.8	*318, 204, 212*	
Heat of transition (kcal/mole)	0.3835	*92*	
Heat of sublimation (kcal) at −63.8°	5.64, 5.57	*331, 143, 168*	
Heat of fusion (kcal)	1.201	*92*	*168, 331*
Free energy of formation, 1 atm, 25°, (cal/mole)	235,000	*331*	
Heat of formation, gas, 1 atm, 25°, (cal/mole)	262,000	*331*	
Heat capacity	See references:	*89, 90, 92, 208, 268*	
Entropy, gas, 1 atm, 25°	69.43, 69.6	*92, 331*	*329*

Density							
Gas at 20°C (gm/liter)	6.093 at 753.5 mm					*271*	
Solid (gm/ml)	2.683	2.51				*168*	
Temperature (°C)	−195	−50					
Liquid (gm/ml)	1.878	1.819	1.787	1.722	1.37	*2, 212, 237, 168, 242*	*204*
Temperature (°C)	−50	−45	−39	−20	20		
Critical density (gm/ml)	0.74, 0.73, 0.7517					*318, 204, 4*	
Solubility in water, cm^3 SF_6 per cm^3 H_2O	0.055	0.076				*97*	
Temperature (°C)	25	14.9					
Solubility in nitromethane, cm^3 gas per cm^3 liquid	0.377	0.363				*97*	
Temperature (°C)	25	19.35					
Specific magnetic susceptibility	$(-0.300 \pm 0.003) \times 10^{-6}$					*144*	
Surface tension (dyne/cm)	11.63	8.02				*237*	*284*
Temperature (°C)	−50	−20					
Dielectric constant, 27.5°	1.00191	1.00123	1.00034			*99*	*188*
Pressure (mm)	708	457	131				
Ionization potential (ev), 1st electron	19.3					*112*	
From spectrum	16.15					*295, 231*	
Calculated	20.1					*80*	
Viscosity of gas, cgs units	1.537×10^{-4}	1.871×10^{-4}				*81*	
Temperature (°C)	22.5	100					
Collision diameter of molecule, determined from viscosity	4.77 Å					*81*	

and 1.0% inerts while the refined product contained 99.8% SF_6, $SF_4 + S_2F_2$ 8 ppm and 0.2% inerts (*190*).

The gas is colorless, odorless, nontoxic, and inert. It is not changed by electrical stress just below the corona point (*82*), but it is decomposed slowly by spark-over or corona electrical discharge (*82*, *272*) giving lower fluorides of sulfur and fluorides of the metals used as the electrodes. It does not react with water or with a basic solution but it does react vigorously with a hot alkali metal. The gas is not toxic; however, it has some depressant action upon the central nervous system (*45*) and has mild anesthetic properties (*312*). In spite of this, rats may live in an atmosphere of 80% SF_6 and 20% O_2 for periods up to one day with no signs of poisoning (*187*).

Sulfur hexafluoride is sold in cylinders containing 100 lb of the material at about $3 per lb (1959 price). It is used as the electrical insulator in coaxial cables, high voltage X-ray transformers, and high voltage generators (*35*, *211*). Its availability is a stimulus to research dealing with the substance. Many studies use the substance because it is inert or because it is made up of nearly spherical molecules. There is also much theoretical interest in its structure and in the nature of the chemical bond involved. Many studies are related to its usefulness as an electrical insulator.

The first work on sulfur hexafluoride as an electrical insulator was reported by Watson and Ramaswamy in 1934 (*317*). Many other studies have followed (*1*, *15*, *17*, *31*, *35*, *38*, *42*, *43*, *53*, *55*, *69*, *82*, *105*, *107*, *119*, *148–154*, *203*, *240*, *241*, *272*, *293*, *315*, *316*, *323*, *335*). The high dielectric strength of the gas results from the tendency of the molecules to capture electrons easily, thereby preventing a "cascade breakdown" (*1*, *15*, *272*). There is a resonance capture of electrons of about 2 ev energy to form SF_6^- and SF_5^- in about equal amounts (*1*). F^- is also formed easily (*316*). Bombarding electrons of much higher voltage may form positive ions but not SF_6^+. Appearance potentials for positive ions as observed by a mass spectrometer are SF_5^+ 15.9 volts, SF_4^+ 18.9 volts, SF_3^+ 20.1 volts, SF_2^+ 26.8 volts, SF^+ 31.3 volts, F^+ 35.8 volts, S^+ 37.3 volts, SF_4^{++} 40.6 volts, and SF_2^{++} 46.5 volts (*68*). The lack of a parent peak is commonly found for fluorides. Apparently a mass spectrometer operating with negative ions would be a desirable tool for studies of fluorides.

Physical properties of sulfur hexafluoride are listed in Table I. These include various values of the critical constants. Several excellent studies of the critical phenomena have been made to learn whether the predictions of Harrison and Mayer (*125*) are correct. They suggested in 1938 that there could be a range of temperature above the observed critical point (disappearance of meniscus) in which the slope of pressure versus volume isotherms is zero. Their arguments have been criticized by Zimm (*334*) in

1951 and Mayer (*200*) has agreed that Zimm's arguments are as plausible as those of Harrison and Mayer. Sulfur hexafluoride has been chosen by Schneider and co-workers (*4, 204*) and by Wentorf (*318*) as a test substance. The latter has found that a liquid meniscus can be observed at 45.64° but not at 45.66°. The pressure versus volume isotherms have regions of zero slope up to 45.68° but not higher. The observed ranges of zero slope are shown in Table II.

TABLE II

RANGE OF SLOPE = 0 IN P VERSUS VOLUME ISOTHERMS OF SF_6 (*318*)

Temperature (°C)		45.52	45.62	45.64	45.66	45.68
Range,	From	1.188	1.212	1.225	1.24	1.26
Units = ml/gm.	To	1.591	1.563	1.550	1.53	1.49
Pressure (atm)		37.084	37.176	37.192	37.21	37.23

These observations are in agreement with the idea that the critical point is a single temperature and not a range of temperatures. It does appear, however, that the coexistence curve for gas and liquid has a very flat top. This is responsible for the rather large differences in critical densities which have been reported. Orthobaric densities for liquid and vapor (Table III) have been determined by Miller *et al.* (*212*) from 9° to 43°. In this work liquid sulfur hexafluoride was found to be a good solvent for nitrogen.

TABLE III

ORTHOBARIC DENSITIES OF SF_6 (*212*)

Temperature (°C)	9	20	30	40	42	43
Density (gm/ml)						
Liquid	1.47	1.37	1.26	1.10	1.07	1.03
Gas	0.14	0.19	0.27	0.35	0.39	0.43

Schneider (*266, 267*) has studied the conduction of sound of 600-kc frequency in the neighborhood of the critical temperature. As the temperature rises the velocity of sound in both liquid and gas decreases up to the critical temperature. At the critical temperature and pressure the velocity is 121.5 meter/sec. Above this temperature the velocity increases. There is a very sharp maximum in the absorption of sound over a range of about 1° with the peak at the critical temperature. From these data the heat capacity at constant volume, near the critical temperature, has been calculated (*268*).

In spite of the fact that the parachor (143.0 at −50°) was at one time considered evidence for a nonsymmetrical structure (*237*) this evidence was questioned (*284*, *243*) and it now appears certain that the fluorine atoms in SF_6 are at the corners of a regular octahedron, the S-F distance being close to 1.56 Å (*5*, *28*, *33*, *89*, *102*, *176*, *234*). It is considered that 3*d* orbitals are used in bond formation and several theoretical papers deal with the nature of the S-F bond (*58*, *59*, *60*, *80*, *103*, *142*, *274*). The force constant, 0.344 megadyne/cm, obtained from vibration data corresponds to an S-F distance of 1.56 Å (*5*). Studies of the Raman and infrared spectrum (*83*, *89*, *102*, *176*, *177*, *260*, *329*, *332*) indicate that SF_6 belongs to the O*h* point group. The spectra are consistent with the regular octahedral structure. The nmr spectrum for fluorine in SF_6 consists of a single peak (*118*) such as would result from a symmetrical molecule.

Intermolecular forces involving sulfur hexafluoride molecules have been discussed in several papers (*91*, *121*, *122*, *194*, *250*, *296*). Other studies include: (a) molecular volume (*254*), (b) stopping of alpha particles (*16*, *117*), (c) transfer of energy by collision (*205*), (d) mutual diffusion of H_2 and SF_6 (*291*), (e) mutual solubilities of gases, including SF_6, in water (*197*), (f) salting out of dissolved gases (*219*), (g) compressibility (*193*) (h) Faraday effect (*161*), (i) adsorption on dry lyophilized proteins (*14*), (j) effect of pressure on electronic transitions (*231*), (k) thermal relaxation of vibrational states (*232*), (l) ultraviolet spectrum (*295*), (m) solubility in a liquid fluorocarbon (*230*).

The chemically inert character of sulfur hexafluoride is responsible for the almost complete lack of exchange of fluorine atoms between SF_6 and HF (*249*). It does react with hot alkali metals, however, and a study has been made of the rate of reaction of Na atoms with SF_6 gas using the sodium diffusion flame technique. The rate constant at 247° is 2.23×10^{-13} cm^3 $mole^{-1}$ sec^{-1} and the energy of activation for the reaction $SF_6 + Na \rightarrow SF_5 + NaF$, is about 37 kcal. A film of sodium on a glass wall does not react with SF_6 at room temperature. The reaction sets in at about 200° (*57*). The fluorides, SF_6, SF_4, and S_2F_2, have no effect upon the viscosity of liquid sulfur in the range 180–195° (*93*). Sulfur hexafluoride forms a solid hydrate which has a crystal constant of 17.21 Å. It decomposes just above 0° (*285*).

Sulfur hexafluoride accelerates the pyrolysis of paraffin hydrocarbons (*164*), lowers the octane number of gasoline containing lead tetraethyl (*189*), removes silicon from a platinum catalyst when heated to 800 to 1000° (*206*) and catalyzes the reaction of ammonia with a ketone and aldehyde to give a substituted pyridine (*196*). It may be used at high pressure to fill a fuse. When the fuse "blows" an arc is prevented (*210*).

B. DISULFUR DECAFLUORIDE

By the sublimation of sulfur hexafluoride in 1933 Denbigh and Whytlaw-Gray (*66, 67*) found a small liquid residue which they identified as S_2F_{10}. From 20 liters of crude SF_6 gas they recovered only about 20 ml of S_2F_{10} vapor. This method of preparation has been confirmed by others (*34, 100, 101, 269, 270, 307*). The substance is a colorless volatile liquid which has a surface tension of 13.9 dyne/cm at 0°C. From its vapor pressure, $\log_{10} P_{mm} = 7.95 - 1530/T$, its heat of vaporization is calculated to be 7000 cal/mole (*67*). Liquid S_2F_{10} has a specific electrical conductivity somewhere between 10^{-12} and 10^{-14} $\text{ohm}^{-1}\ \text{cm}^{-1}$, a dielectric constant of 2.030 at 10° and a density of 2.081, 2.054, and 2.028 gm/ml at 4°, 12°, and 20°, respectively. Its dipole moment is 0 (*155*). Each sulfur atom is linked octahedrally to five fluorine atoms at a distance of 1.56 Å and to the other sulfur atom at a distance of 2.21 Å (*7, 129*).

Disulfur decafluoride has to a limited degree the inert character of sulfur hexafluoride. It does not react at 20° with water, mercury, or copper but it does react slowly with a solution of sodium hydroxide. It reacts with hot mercury or copper (*67*). When the gas is passed through a hot tube at about 400° it decomposes according to the equation $S_2F_{10} \rightarrow SF_6 + SF_4$ (*100, 190, 269, 270*). Within the range 433–455°K the reaction is homogeneous and of first order with a rate constant described by the equation, $K = 2.99 \times 10^{20}\ e^{-49{,}200/RT}$. The very high frequency factor suggests a chain reaction (*307*). The compound is more toxic than phosgene. Lung injury and death within 18 hr occur to rats placed in an atmosphere containing one part per million of S_2F_{10} (*187*). The 50% lethal dose, by intravenous injection in dogs as a lecithin emulsion, is 5.79 mg/kg of body weight (*259*).

C. SULFUR TETRAFLUORIDE

Sulfur tetrafluoride was identified in 1929 by Fischer and Jaenckner (*96*) who produced the gas by heating a mixture of sulfur, cobalt trifluoride, and calcium fluoride (this inert material was used to reduce the vigor of the reaction and to prevent explosions). The compound has also been obtained by: (a) burning sulfur in fluorine (*34, 100, 101, 190, 270*), (b) heating S_2Br_2 with IF_5 (*265*) (c) combustion of CS_2 in fluorine highly diluted by nitrogen (*280*), (d) decomposition of CF_3SF_5 into $CF_4 + SF_4$ by spark-over electrical discharge (*279*), and, perhaps, (e) spark-over electrical discharge in sulfur hexafluoride (*272*). (This process gives one or more lower fluorides of sulfur but it is not certain that it gives SF_4).

The substance is colorless. It fumes in air, has an irritating bad odor (*96*), a surface tension at 200°K of 25.70 dynes/cm, and a heat of vaporization at the boiling point of 6320 cal/mole (*34*). A high Trouton constant suggests that the liquid is somewhat associated. Equations showing the effect of temperature upon various physical properties are given below (*34*).

Vapor pressure, 160–224°K: $\log_{10} P_{\text{mm}} = 8.8126 - 1381/T$

Surface tension, 190–230°K: $\gamma\ (\text{dyne/cm}) = 61.36 - 0.1783T$

Density, 170–200°K: $d\ (\text{gm/ml}) = 2.5471 - 0.003147T$

Coefficient of Cu expansion, 170–200°K: $= 0.00170$

The infrared and Raman spectra indicate that the molecule has no symmetry (point group C_{2v}) (*70*). This structure is confirmed by the nmr spectrum for liquid SF_4 at $-100°$. There are two equally strong sets of triplet peaks which suggest two pairs of identical fluorine atoms. As the SF_4 is warmed, the triplets become broad single peaks above $-94°$ and at higher temperatures the two broad peaks merge into one. This effect indicates a rapid exchange of fluorine atoms (*56*). The structure suggests that hybrid sp^3d-orbitals are used for bond formation giving a trigonal bipyramid with an unshared electron pair occupying one of the "belt" positions (*56*). Before the above studies were made, the structure was thought to be tetrahedral (*175*, *198*).

Sulfur tetrafluoride reacts with a little water to give SOF_2 and HF (*70*). It is readily absorbed by a solution of sodium hydroxide (*100*, *270*) and at first it was thought to react with mercury (*96*). Later work has shown that the SF_4 does not react with mercury but that the crude material contains reactive impurities which can be removed by shaking with mercury (*191*). Sulfur tetrafluoride combines with boron trifluoride to form the compound $SF_4 \cdot BF_3$ which sublimes at about 80° under a pressure of 1 atm. When this compound is heated with sodium fluoride the boron trifluoride reacts to give $NaBF_4$. Sulfur tetrafluoride combines with arsenic pentafluoride to form $SF_4 \cdot AsF_5$ (sublimes at 190°) and with SbF_5 to form $SF_4 \cdot SbF_5$ (melts at 245°). These substances may be donor-acceptor addition compounds (*6*) but it is thought that $SF_4 \cdot BF_3$ is composed of the ions SF_3^+ and BF_4^- (*56*).

Reviews of the chemistry of sulfur tetrafluoride may be found in some of the references (*34*, *37*, *211*, *253*, *306*).

D. Disulfur Difluoride ("Sulfur Monofluoride") and Sulfur Difluoride

It is well known that the fluorination of sulfur produces one or more lower fluorides which are unstable at room temperature and deposit sulfur on the walls of the container. In 1923 Centnerzwer and Strenk (*46*) obtained such a product by heating a mixture of sulfur and silver fluoride. From the density and analysis of the gas (not distilled to isolate the various substances present) they chose S_2F_2 as the formula. They later (*47*) reported a melting point of −105.5° and a boiling point of −99° but found that a liquid remained even at room temperature when the product boiled away. Strenks (*292*) found that SiF_4 was present in his crude product and concluded that the earlier physical constants should not be trusted. Ruff (*253*), in a preliminary report on incomplete work of Jaenkner, said in 1933 that S_2F_2 boils at −38.4° and freezes at −120.5°, and that SF_2 (the first report of this compound) boils at about −35°. He also said that because of the proximity of boiling points, the compounds SF_4, SF_2, S_2F_2, and SOF_2 are difficult to separate from each other (*253*). In this work neither SF_2 nor S_2F_2 was obtained pure. Trautz and Ehrmann (*306*) found the product obtained from sulfur and silver fluoride to be a mixture, but they were unable to isolate a pure sample of S_2F_2. They obtained a mixture which they thought to be SF_2 and S_2F_2. Dubnikov and Zorin (*75*) described in 1947 various methods of producing crude mixtures of SF_2 and S_2F_2 but did not isolate either compound. Still others (*82, 156, 199, 270, 272*) have worked with these lower fluorides of sulfur but no one has clearly reported isolating either SF_2 or S_2F_2.

An infrared spectrum has been reported for S_2F_2 (*199*) and infrared spectra have been used in the Bell Laboratories to identify both SF_2 and S_2F_2 as products of the decomposition of SF_6 by electrical discharge (*82*). It is not said how the control samples of SF_2 and S_2F_2 were prepared nor are the spectra given. The products, SF_2 and S_2F_2 are described as being fairly stable when pure but readily hydrolyzed by a trace of water to give HF and SO_2 (sulfur not mentioned) (*82*). These lower fluorides are absorbed by NaOH solution (*46, 306*), and hydrolysis by water is said to give HF, H_2SO_3, and S (*292*) The gas is said to attack mercury (*306*) and, when pure, not to attack mercury (*47*). It is poisonous (*292, 82*).

If the reader is now confused about S_2F_2 and SF_2, he is in the same position as the writer.

III. Sulfur Oxyhalides Containing Fluorine

A. Oxyhalides Containing One Atom of Sulfur per Molecule

1. *Thionyl Fluoride,* F_2SO

Thionyl fluoride was first prepared by Meslans (*207*) in 1896 and four years later it was described in more detail by Moissan and Lebeau (*216, 217*) who produced it by the reaction of thionyl chloride with fluorine or (preferably) arsenic trifluoride. Steinkopf and Herold also used arsenic trifluoride (*288*) Other reactions which have been used to produce thionyl fluoride are: (a) refluxing thionyl chloride over antimony trifluoride containing some antimony pentachloride (*21*) (b) heating together thionyl chloride and hydrogen fluoride in the presence or in the absence of a catalytic amount of antimony pentafluoride (*314*, *320*) (c) contacting vanadium pentafluoride with sulfur dioxide at room temperature (98% yield of SOF_2) (*50*) (d) the action of fluorine upon cold sodium thiosulfate (*229*, *239*) (low yield of SOF_2), (e) heating together S_4N_4, CuO, and HF in a sealed bomb at 100° (*255*), (f) heating together iodine pentafluoride and thionyl chloride (*165*) (g) passing thionyl chloride vapor over potassium fluorosulfinate, KSO_2F, at 150° (*273*).

Thionyl fluoride is a colorless gas having an irritating odor. The substance does not attack glass (at 20°) or mercury, but it reacts rather slowly with water to give hydrofluoric and sulfurous acids. With ammonia it gives $OS(NH_2)_2$ (*207*). It reacts with hot glass but is inert toward iron at red heat and toward several other metals at temperatures up to 125° or more (*21*).

The vapor pressure of the liquid is given by the equation $\log_{10} P_{mm} = 30.333 - 1908.4/T - 8.1053 \log_{10} T$. The critical temperature and pressure are 89.0° and 55.3 atm, respectively (*21*). Infrared and Raman spectra have been interpreted (*12*, *233*, *329*) and the microwave spectrum gives moments of inertia consistent with the structure: $r_{SO} = 1.412 \pm 0.001$ Å, $r_{SF} = 1.585 \pm 0.001$ Å, $\angle FSF = 92°\,49' \pm 5'$, $\angle OSF = 106°\,49' \pm 5'$. The Stark effect has also been studied (*95*). By use of method of linear combination of atomic orbitals (LCAO), Moffitt has concluded that the SO bond in thionyl fluoride and in sulfuryl fluoride is a double bond (*214*).

2. Thionyl Chlorofluoride, SOClF

When Booth and Mericola (1940) allowed thionyl chloride to react with antimony trifluoride containing some antimony pentachloride they obtained as products both thionyl fluoride and thionyl chlorofluoride, SOClF (*21*). The compound was also produced in the laboratory of Otto Ruff (1937) but the work was not published until 1951. For this work iodine pentafluoride was heated with thionyl chloride (*165*).

Thionyl chlorofluoride is somewhat more reactive than thionyl fluoride but less so than thionyl chloride. It reacts with mercury and is readily hydrolyzed. Upon standing at room temperature for several months it disproportionates to a considerable extent into thionyl chloride and thionyl fluoride. The reactivity of SOClF at elevated temperatures may be due largely to $SOCl_2$ formed by disproportionation (*21*). When thionyl chlorofluoride is chilled quickly it congeals to a glass (*165*) but it can be made to form crystals which melt at −139.5°. The influence of temperature upon density and vapor pressure are shown by the equations:

$d(\text{gm/ml}) = 1.576 - 0.00224\,t$ Ref. *165*

$\log_{10} P_{\text{mm}} = 7.0466 - 12782.2/T + 0.1268 \log_{10} T$ Ref. *21*

$\log_{10} P_{\text{mm}} = 7.83 - 1409/T$ Ref. *165*.

where t is in degrees centigrade and T is in degrees Kelvin.

3. Thionyl Tetrafluoride, SOF_4

Moissan and Lebeau (1902) mixed fluorine and thionyl fluoride at room temperature and obtained a new product. From the change in pressure during the reaction they considered the product to have the formula SOF_4. They did not definitely identify the substance (*217*). The substance was prepared and studied in the laboratory of O. Ruff in 1937 but the work was not published until after World War II. The reaction of F_2 with SOF_2 took place in the presence of platinum at about 150° (*165, 174*). Thionyl tetrafluoride has also been produced from SOF_2 and F_2 in a copper tube reactor packed with a fluorinated copper, AgF_2 catalyst (*78*).

Thionyl tetrafluoride is a colorless gas which reacts with water rapidly forming SO_2F_2, HF, H^+, and SO_3F^-. With NaOH solution it gives F^- and SO_3F^-. It reacts slowly with mercury at room temperature to give mercurous fluoride and thionyl fluoride (*78, 165*). The density and vapor pressure of SOF_4 are given by the equations:

$d(\text{gm/ml}) = 1.653 - 0.00360\,t(^\circ\text{C})$ Ref. *165*

$d(\text{gm/ml}) = 2.6963 - 4.1121 \times 10^{-3}\,T(^\circ\text{K})$ Ref. *78*

$\log_{10} P_{\text{mm}} = 7.76 - 1092/T$ Ref. *165*

$\log_{10} P_{\text{mm}} = 7.2349 - 8.5958 \times 10^{2}/T - 2.6275 \times 10^{4}/T^{2}$ Ref. *78*

P = vapor pressure of liquid; heat of vaporization = 5090 cal/mole

The mass spectrum is known (*78*) and there is only one nmr "line" for fluorine in the nmr spectrum of thionyl tetrafluoride at room temperature (*79*). This probably means that there is a rapid exchange of fluorine atoms within the molecule.

4. Pentafluorosulfur Hypofluorite, F_5SOF

In 1955 Dudley, working with Cady and Eggers, obtained pentafluorosulfur hypofluorite by the reaction of fluorine, in excess, with thionyl fluoride, or sulfur dioxide, at 200° in the presence of copper coated with fluorides of silver (*78*). It is probable that thionyl tetrafluoride is an intermediate in the process and that it combines with fluorine to give F_5SOF.

Pentafluorosulfur hypofluorite is a very reactive colorless gas having an odor resembling that of oxygen fluoride. It reacts with aqueous KI and aqueous KOH according to the equations:

$$F_5SOF + 2I^- + H_2O = SO_2F_2 + 2HF + I_2 + 2F^-$$
$$F_5SOF + 6OH^- = 5F^- + \tfrac{1}{2}O_2 + 3H_2O + SO_3F^-$$

Equations for vapor pressure and density of the liquid are:

$$\log_{10} P_{mm} = 6.03633 - 4.2035 \times 10^2/T - 7.836 \times 10^4/T^2$$
$$d(\text{gm/ml}) = 2.788 - 3.722 \times 10^{-3}T$$

There are two widely separated "lines" for fluorine in the nmr spectrum of F_5SOF. As would be expected for this molecule, the line at the lower magnetic field is only one fifth as strong as the other. Since the five fluorine atoms attached to the sulfur cause only one "line" at room temperature it is probable that a rapid exchange occurs among these five atoms. At a lower temperature this "line" should break into a complex structure (*78*, *79*).

Electron diffraction by pentafluorosulfur hypofluorite is consistent with the following structural features for the molecule: $r_{SF} = 1.53$ Å, $r_{OF} = 1.43$ Å, $r_{SO} = 1.64$ Å, ∠FSF = about 90°, ∠SOF = about tetrahedral, somewhat greater than 103°, ∠FSO (opposed F and O atoms) slightly different from 180°. The structure about the sulfur atom is essentially octahedral (*61*).

5. *Sulfuryl Fluoride*, SO_2F_2

Moissan and Lebeau (1901) produced sulfuryl fluoride by the combination of sulfur dioxide with fluorine (*217*). Other processes which have been used to produce the gas are: (a) the thermal decomposition of barium fluorosulfonate or certain other fluorosulfonates (*133*, *221*, *303*), (b) the reaction of sulfur dioxide with chlorine and hydrogen fluoride in the presence of activated charcoal at 400° (*11*), (c) the reaction of sulfur dioxide and chlorine with potassium or sodium fluoride at 400° (*328*), (d) the disproportionation of sulfuryl chlorofluoride at 300–400° (*328*), (e) the reaction of sulfuryl chloride with a mixture of antimony trifluoride and antimony pentachloride at about 250° (*86*), (f) the reaction of sulfur dioxide with silver difluoride (*86*), (g) the reaction of thionyl fluoride with oxygen in an electrical discharge (*314*), (h) electrolysis of a solution of fluorosulfonic acid in hydrogen fluoride (*264*), (i) the reaction of fluorine with sodium sulfate, sodium sulfite or sodium thiosulfate (*229*, *239*), (j) the reaction of hydrogen fluoride with sulfuryl chloride (*320*).

In many ways sulfuryl fluoride is much like sulfur hexafluoride. Its rate of hydrolysis even in a basic solution is slow; its boiling point is low; it is stable (*217, 306*), but decomposes slowly at about 1000° to give SOF_2 (*221*); it is a very good gaseous electrical insulator (*17, 31*). Although the hydrolysis in water is very slow, the reaction with highly concentrated hydrofluoric acid is almost instantaneous (*320*). The hydrolysis in alcoholic potassium hydroxide is more rapid than in aqueous potassium hydroxide (*217*).

The physical properties of sulfuryl fluoride are not well known. As one may see from Table VI there is considerable doubt about its melting and boiling points. Many other physical constants have not been measured at all. Over the temperature range $-155°$ to $-83°$ the vapor pressure is represented by the equation $\log_{10} P_{\mathrm{mm}} = 7.593 - 1023/T$ and the boiling point obtained from this equation is $-56.2°$ (*229*). Good studies of the Raman (*12*) and infrared spectra (*12, 238*) have been made. An electron diffraction study gives scattering consistent with the structure: $r_{\mathrm{SF}} = 1.56 \pm 0.02$ Å, $r_{\mathrm{SO}} = 1.43 \pm 0.02$ Å, $\angle \mathrm{FSO} = 105 \pm 2°$, $\angle \mathrm{FSF} = 100 \pm 10°$, $\angle \mathrm{OSO} = 130 \pm 10°$ (290). The microwave spectrum gives a dipole moment of 0.228 ± 0.004 Debye units and is consistent with a C_{2v} symmetry corresponding to $r_{\mathrm{SF}} = 1.570 \pm 0.01$ Å, $r_{\mathrm{SO}} = 1.370 \pm 0.01$ Å, $\angle \mathrm{FSF} = 92° 47' \pm 30'$ and $\angle \mathrm{OSO} = 129° 38' \pm 30'$ (*98*). Molecular orbital (LCAO) calculations assuming the use of 3*d* orbitals of the sulfur atom indicate that the SO bond is essentially a double bond (*214*).

6. *Sulfuryl Chlorofluoride*, SO_2ClF

In 1936 Booth and Hermann (*19*) reported the preparation of sulfuryl chlorofluoride by the reaction at 300° of sulfuryl chloride with antimony trifluoride containing some antimony pentachloride. Others have used a similar procedure (*86, 113*). The compound has also been produced by heating together at 80° sulfuryl chloride and ammonium fluoride (*328*), by the reaction of sulfuryl chloride with CoF_3, MnF_3, or AgF_2 (*201*), and by the reaction of pyrosulfuryl chloride, $S_2O_5Cl_2$, with iodine pentafluoride (*265*). Sulfuryl chlorofluoride is colorless and intermediate in reactivity between SO_2Cl_2 and SO_2F_2. It reacts with water but not with glass, mercury, or brass at room temperature (*19*). It decomposes at 300–400° in metal apparatus to give SO_2, Cl_2, and SO_2F_2 (*328*). At 0° its surface tension is 17.2 dyne/cm. (*19*).

7. *Sulfuryl Bromofluoride*, SO_2BrF

In 1951 Jonas reported the preparation of sulfuryl bromofluoride in the laboratory of O. Ruff in 1937. The substance was produced by the reaction of: (a) BrF_3 with CCl_3SO_2Cl, (b) sulfur dioxide with bromine and bromine trifluoride. It is very stable but reacts vigorously with water. The density of the solid at liquid air temperature is 3.16 gm/ml and for the liquid the density may be obtained from the equation

$$d = 2.175 - 0.00289\ t(^\circ\mathrm{C}).$$

Vapor pressures correspond to the equation

$$\log_{10} P = 8.03 - 1610/T\ (\mathit{165}).$$

8. *Fluorine Fluorosulfonate*, SO_3F_2

Dudley, working with Cady and Eggers, in 1955 obtained fluorine fluorosulfonate by combining sulfur trioxide with fluorine at about 200°, or by the reaction of fluorine with sulfamic acid. The compound is colorless and it has an odor resembling that of oxygen fluoride. It reacts with a solution of sodium hydroxide and with potassium iodide solution according to the equations:

$$SO_3F_2 + 2OH^- = SO_3F^- + F^- + H_2O + \tfrac{1}{2}O_2$$
$$SO_3F_2 + 2I^- = SO_3F^- + F^- + I_2$$

The influence of temperature upon vapor pressure and density of the liquid are represented by the equations (*76*):

$$\log_{10} P_{\mathrm{mm}} = 6.56476 - \frac{6.2687 \times 10^2}{T} - \frac{6.3906 \times 10^4}{T^2}$$
$$d = 2.4314 - 0.00325\ T$$

There are two doublet peaks of equal intensity in the nmr spectrum (*79*). This fact together with the chemical reactions given above is in accord with the structure

$$O\overset{O}{\underset{F}{S}}OF$$

B. Compounds Containing Two or More Atoms of Sulfur Per Molecule

1. *Bis(pentafluorosulfur) Peroxide*, F_5SOOSF_5

This compound was first prepared by J. W. Dale and D. A. MacLeod of the Defense Research Chemical Laboratories, Ottawa, Canada. The only publication is that of Harvey and Bauer who determined its structure by electron diffraction and who used the name "disulfur decafluorodioxide." The substance was obtained as a minor product of the combustion of sulfur in fluorine. It is diamagnetic and has the structure of a peroxide with the structural parameters: $r_{SF} = 1.56 \pm 0.02$ Å, $r_{OO} = 1.47 \pm 0.03$ Å, $r_{SO} = 1.66 \pm 0.05$ Å, $\angle SOO = 105 \pm 3^\circ$, dihedral angle SOOS (looking along an axis through the two O atoms) = 107 ± 5°. The SF_6 groups are octahedral (*128*). The value of r_{SO} in this compound is much larger than that in SOF_2 or SO_2F_2.

2. Pyrosulfuryl Fluoride (Disulfuryl Fluoride), $S_2O_5F_2$

In 1951 Hayek and Koller produced pyrosulfuryl fluoride by refluxing sulfur trioxide with antimony pentafluoride (*136*). The compound has also been obtained by: (a) the thermal decomposition of a product made by the combination of sodium fluoride with sulfur trioxide (*132*), (b) the reaction of iodine pentafluoride with sulfur trioxide (*265*), (c) the thermal decomposition of certain fluorosulfonates (*133*), (d) heating together HSO_3F and As_2O_5 (*135*), (e) the reaction at room temperature of sulfur trioxide with vanadium pentafluoride (*50*), (f) mixing 60–98% sulfuric acid at 25° with solid [$Ca(S_2O_6F)_2$?] formed by adding an excess of sulfur trioxide to calcium fluoride at 100–300° (*221, 222*).

Pyrosulfuryl fluoride is a colorless liquid which hydrolyzes rather slowly to give HSO_3F. It is not very soluble in cold concentrated sulfuric acid but is soluble in carbon tetrachloride or benzene. It is poisonous. When heated to about 400° it decomposes into sulfuryl fluoride and sulfur trioxide (*134, 135, 136, 221*). The equation for its vapor pressure is

$$\log_{10} P_{\mathrm{mm}} = 8.015 - 1662/T.$$

This gives a heat of vaporization of 7600 cal/mole (*50*). The infrared spectrum and the nmr spectrum are consistent (*221*) with the structural formula

$$\mathrm{F\overset{O}{\underset{O}{S}}O\overset{O}{\underset{O}{S}}F.}$$

3. Pyrosulfuryl Chlorofluoride, S_2O_5ClF

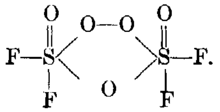
Engelbrecht (1953) produced pyrosulfuryl chlorofluoride by the reaction of pyrosulfuryl chloride with silver fluoride at about 80°. The reaction also gave some sulfuryl chlorofluoride.

Pyrosulfuryl chlorofluoride is a colorless liquid which hydrolyzes slowly and does not attack dry glass or mercury. From the vapor pressures the heat of vaporization at the boiling point is 8070 cal/mole (*87*).

Vapor pressure (mm of Hg)	49.2	68.0	133.0	319.2	567.7	799.4
Temperature (°C)	32.7	40.0	53.1	73.9	90.7	101.7

4. $S_2O_5F_4$, *Monoperoxytetrafluorodisulfur(VI) oxide*

In 1952 Wannagat and Mennicken (*314*) described the reaction of oxygen with thionyl fluoride in an ozonizer at −50—−60°. Upon distilling the product, they found in addition to unused reactants the substances sulfuryl fluoride, $S_2O_5F_4$ and an impure material having approximately the composition $S_2O_6F_2$. The yields were small and the work was difficult because of the small amounts of materials involved. $S_2O_5F_4$ decomposes above −20° into SO_2F_2 and O_2. It oxidizes I^- to I_2. It may have the structure



5. *Peroxydisulfuryl Difluoride*, $S_2O_6F_2$

The product of Wannagat and Mennicken (*314*) (see Section III.B.4) contained a small amount of material which was not obtained pure, but had a composition close to $S_2O_6F_2$. The properties of this material differed considerably from those of a pure form of $S_2O_6F_2$, peroxydisulfuryl difluoride, reported in 1957 by Dudley and Cady (*77*). It is, therefore, not certain that the two substances are the same. The compound is easily produced by the reaction of fluorine with an excess of sulfur trioxide at about 250° or by the reaction of fluorine fluorosulfonate with sulfur trioxide.

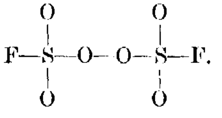
Peroxydisulfuryl difluoride is a colorless liquid which reacts with water according to the equation:

$$S_2O_6F_2 + H_2O = 2SO_3F^- + 2H^+ + \tfrac{1}{2}O_2.$$

When reacting with potassium iodide solution, one mole of $S_2O_6F_2$ liberates one mole of iodine. Equations for the vapor pressure and density are:

$$\log_{10} P_{\mathrm{mm}} = 5.49916 - 1.2925 \times 10^2/T - 2.5921 \times 10^5/T^2$$
$$d(\mathrm{gm/ml}) = 2.3959 - 2.434 \times 10^{-3}\, T$$

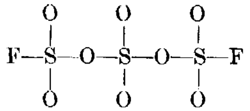
The infrared and nmr spectra are in accord with the structural formula



$$\mathrm{F{-}\underset{O}{\overset{O}{S}}{-}O{-}O{-}\underset{O}{\overset{O}{S}}{-}F}.\quad (77)$$

6. *Trisulfuryl Fluoride*, $S_3O_8F_2$

A compound of the above empirical formula and presumably of the structure



$$\mathrm{F{-}\underset{O}{\overset{O}{S}}{-}O{-}\underset{O}{\overset{O}{S}}{-}O{-}\underset{O}{\overset{O}{S}}{-}F}$$

was described by Lehmann and Kolditz in 1953 (*186*). To prepare the substance they saturated liquid sulfur trioxide with boron trifluoride and to the resulting solution then added 70% sulfuric acid while keeping the materials cooled by ice. This released $S_3O_8F_2$ as a separate liquid phase which could be removed by distillation. They also formed the substance by the destructive distillation of $KBF_4 \cdot 4SO_3$ at about 65°.

Trisulfuryl fluoride is a colorless liquid which hydrolyzes slowly in KOH solution according to the equation

$$S_3O_8F_2 + 4OH^- = 2SO_3F^- + SO_4^= + 2H_2O.$$

This reaction indicates that the two fluorine atoms are not attached to the same sulfur atom in the molecule (*186*).

IV. Fluorooxyacids of Sulfur

A. Fluorosulfonic Acid, Its Salts and Its Esters

1. *Fluorosulfonic Acid,* HSO_3F

In 1892 Thorpe and Kirman reported the preparation and properties of fluorosulfonic acid. They condensed together sulfur trioxide and hydrogen fluoride and removed the excess of the latter by sweeping with a stream of carbon dioxide (*298*). The acid is now made commercially by combining sulfur trioxide with hydrogen fluoride (*157, 158, 159, 211, 289*). A convenient laboratory method is the distillation of a mixture of potassium acid fluoride and oleum in glass apparatus (*211*). Other procedures which have been used are: (a) distilling a mixture of a fluoride and oleum (*163, 213, 256, 302, 304*), (b) distilling a mixture of HSO_3Cl and NH_4F or a fluoride of an alkali or alkaline earth metal (*160*), (c) adding sulfur trioxide to a mixture containing sulfuric and hydrofluoric acids (*311*), (d) adding hydrogen fluoride to chlorosulfonic acid (*320*).

The anhydrous acid is a colorless liquid which fumes in air and dissolves readily in water. In solution the acid is highly ionized as shown by electrical conductivity (*326*). The SO_3F^- which is formed at first, reacts eventually to give $SO_4^=$ and HF. When a little water is mixed with fluorosulfonic acid, an equilibrium of the type $H_2SO_4 + HF \rightleftharpoons HSO_3F + H_2O$ is established. This reaction has been studied by Traube and Reubke (*305*) and by Lange (*181*). Thorpe and Kirmann (*298*) found a boiling point of the acid of 162.6° (the value still given in the literature) and they considered that slow decomposition occurred at the boiling point to give, presumably, sulfuryl fluoride and sulfuric acid. In contrast to this Ruff (*252*) found the acid to be stable up to 900°C. The anhydrous acid is a poor electrical conductor but it acts as an ionizing solvent. Dissolved KSO_3F, according to studies by Woolf (*327*), is highly ionized in HSO_3F and the high molecular conductivity indicates a charge transfer mechanism of the Grotthus chain type. The self-ionization of the anhydrous acid gives mostly SO_3F^- and a solvated proton. Such ions as H_2F^+ and $S_2O_6F^-$ may also be present. In anhydrous HSO_3F antimony pentafluoride acts as an acid, probably forming SbF_6^- as it does in liquid HF. Other acidic substances are AuF_3, TaF_5, and PtF_4. Among the bases are fluorosulfonates, such as KSO_3F, and the fluorides AsF_3, SbF_3, BrF_3, and IF_5. Even $HClO_4$ is a proton acceptor and, therefore, a base (*327*).

The abnormally high heat of neutralization, 14.46 kcal/mole, of fluorosulfonic acid (*326*) has not been fully explained.

Glass is not appreciably attacked by the liquid acid but the part of a glass container in contact with the vapor over the liquid is attacked slowly. The cold anhydrous acid does not attack S, C, Se, Te, Pb, Ag, Cu, Zn, Fe, Cr, or Mn but it slowly dissolves Hg and Sn. At higher temperatures it dissolves S, Pb, Hg, and Sn rather rapidly. Rubber, cork, wood, and sealing wax are attacked (*209*).

Fluorosulfonic acid is a useful catalyst and reagent for the production of important organic compounds. Uses given in the literature are: (a) a catalyst for the alkylation of hydrocarbons (*71, 127, 162, 286, 297*), (b) a catalyst for the isomerization of hydrocarbons (*39, 192, 247, 248*), (c) a catalyst for "condensation" of various mixtures of organic materials (*163, 166, 283*), (d) a reagent to cause ring closure (*52, 146*), (e) removal of metals from petroleum (*54*), (f) desulfurization of petroleum products (*48*), (g) improvement of viscosity of lubricating oil (*44*), (h) production of esters and salts of fluorosulfonic acid (*41, 180, 184, 246, 252*), (i) an agent to polymerize rosin (*25*), (j) an agent to attack cellulose (*218*), (k) a selective solvent for separating hydrocarbons (*294*), (l) a solvent to absorb and recover hydrogen fluoride used as a catalyst for the alkylation of paraffin hydrocarbons (*126*), (m) a reagent for the production of DDT (*257*), (n) a component of a solution used for the anodic polishing of stainless steel (*333*).

The chemistry of fluorosulfonic acid, its salts and its esters has been reviewed by Lange (*178a*).

2. Fluorosulfonate ion, SO_3F^-

The fluorosulfonate ion is present in aqueous solutions of fluorosulfonic acid or its salts. It hydrolyzes slowly according to the equation $SO_3F^- + H_2O \rightarrow SO_4^= + F^- + 2H^+$. In a slightly alkaline solution the reaction is first order with respect to the fluorosulfonate ion with a heat of activation of 17.9 kcal and an entropy of activation of −31 cal/degree. In acidic solutions the rate is more rapid than in neutral or basic solutions (*258*).

Studies of the infrared (*276, 277*) and Raman spectra (*278*) of fluorosulfonates have been made.

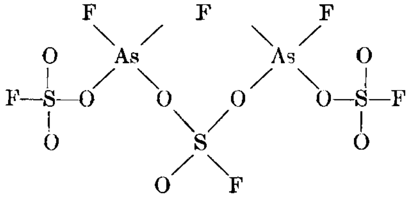
Since the fluorosulfonate ion has the same sort of structure and charge as the perchlorate ion it is not surprising that certain fluorosulfonates are isomorphous with the corresponding perchlorates (*178*, *276*, *321*). Isomorphous salts have been obtained for the anions BF_4^-, SO_3F^-, ClO_4^-, MnO_4^- (*321*).

In general the salts of fluorosulfonate ion are very soluble in water, the only highly insoluble one being that formed by the organic base, nitron (*211*).

3. Salts Containing Fluorosulfonate Ion

A procedure which has been used commonly to prepare fluorosulfonates is the addition of sulfur trioxide to a fluoride. This method was used by Traube in 1913 (*301*, *302*) and has since then been employed by others (*133*, *221*). Even chloryl fluoride, ClO_2F, adds SO_3. The product, chloryl fluorosulfonate, ClO_2SO_3F, is a red liquid at room temperature. It was discovered independently in 1954 by Woolf (*325*) and by Schmeisser and Ebenhöch (*263*). Another convenient method for preparing fluorosulfonates is to add a fluoride of a metal to fluorosulfonic acid and then to distil off hydrogen fluoride (*303*). Fuming sulfuric acid and a fluoride may also be used (*301*, *303*). Sodium chloride and fluorosulfonic acid react when heated to give HCl and $NaSO_3F$ (*252*). In some cases the reaction of sulfur trioxide with a fluoride gives a "double salt." For example, tungsten hexafluoride gives a product which probably is $WF_2(SO_3F)_4$ (*49*). The discoverers, Clark and Emeléus (1957) say that it, like $NbF_3(SO_3F)_2$ and $TaF_3(SO_3F)_2$, is a liquid of low volatility at room temperature and that it hydrolyzes readily. Another method used to produce double salts, such as $AlCl(SO_3F)_2$, $TiCl(SO_3F)_2$, and ZrF_3SO_3F, is the reaction of a chloride of a metal with fluorosulfonic acid (*137*).

Arsenic trifluoride has been found by Engelbrecht *et al.* (*88*) to combine with sulfur trioxide to form a volatile compound $2AsF_3 \cdot 3SO_3$. This has been confirmed by Muetterties and Coffman (*221*) who found that SO_3 and SbF_3 appear to give $Sb(SO_3F)_3$. The nmr spectrum of $2AsF_3 \cdot 3SO_3$ consists of three F^{19} peaks of relative intensity 3:2:1, the peak of intensity 3 corresponding to fluorine bound to sulfur. This suggests the structure:



The substance behaves as a fluorinating and sulfonating agent (*221*).

Melting points for a few fluorosulfonates are given in Table VI (*211, 303*).

The pyrolysis of barium strontium and zinc fluorosulfonates at about 500° produces a gas which is largely sulfuryl fluoride (*221, 303*). By a similar process calcium fluorosulfonate gives sulfur trioxide and only a little SO_2F_2 (*221*).

Infrared spectra are known for the fluorosulfonates of ammonium, sodium potassium, rubidium, and cesium (*276, 277, 278*).

TABLE IV
MELTING POINTS OF FLUOROSULFONATES

Salt	Temperature (°C)	Salt	Temperature (°C)
NH_4SO_3F	245	$RbSO_3F$	304
$LiSO_3F$	360	$CsSO_3F$	292
KSO_3F	311		

Nitrosyl fluorosulfonate, $NOSO_3F$, was produced by Lange (*179*) (1927) by the reaction of N_2O_3 with HSO_3F. It may also be formed by the reaction of BrF_3 with $(NO)_2S_2O_7$ (*324*) or as a by-product of the oxidation of a perfluoroalkane sulfonyl fluoride by an excess of nitrogen dioxide at about 550°. For example, $C_8F_{17}SO_2F$ and NO_2 give $C_7F_{15}COF$ and $NOSO_3F$ (*275*). Nitrosyl fluorosulfonate is a white solid at room temperature. It is very hygroscopic. An impure form of the compound, as obtained by Lange (*179*), begins to soften at about 118° and is completely molten at about 140°.

Nitronium fluorosulfonate, NO_2SO_3F, is formed by the reaction of an excess of nitrogen dioxide with a mixture of sulfur trioxide and bromine trifluoride (Woolf, 1950, *324*) or by the reaction of dinitrogen pentoxide with fluorosulfonic acid (Goddard *et al.*, 1950, *111a*). The compound is a white solid composed of the ions NO_2^+ and SO_3F^-, as shown by its Raman spectrum (*209a*). It melts at about 200° and reacts with water to give H^+, NO_3^- and SO_3F^- ions (*111a*).

4. Esters of Fluorosulfonic Acid

Several aryl esters of fluorosulfonic acid were prepared by Lange (1930) by decomposing an aryldiazonium fluorosulfonate, such as $C_6H_5N_2SO_3F$ at about 100° (*180, 184*). A method for preparing a diazonium fluorosulfonate is to add HSO_3F to an aqueous solution of a diazonium salt and to then remove the precipitated diazonium fluorosulfonate (*145*). Alkyl esters were prepared by Meyer and Schramm (1932) by the reaction of fluorosulfonic acid with an ether or an alcohol. For example, C_2H_5OH and HSO_3F gave $C_2H_5SO_3F$ (*209*). Calfee and Florio produced esters by adding $CH_2{=}CF_2$ or $CHCl{=}CF_2$ to fluorosulfonic acid at a temperature below 30° (*41*). The resulting esters are useful as fumigants for stored grain (*40*).

A few physical constants of some of these esters are given in the literature (*41, 180, 184, 209, 246*).

B. SALTS OF FLUORODISULFURIC ACID

Lehmann and Kolditz (1953) condensed an excess of sulfur trioxide on potassium fluoride and later distilled off the excess at about 35°. White crystals of potassium fluorodisulfate, KS_2O_6F, remained (*185*). Muetterties and Coffman thought that they obtained $Ca(S_2O_6F)_2$ by the action of a large excess of SO_3 upon CaF_2 but they did not analyze the material (*221*).

C. FLUOROSULFINIC ACID AND ITS SALTS

1. *Fluorosulfinic Acid*, HSO_2F?

Seel and Riehl (1955) have studied the system $HF\text{-}SO_2$ and have found a single compound, $HF \cdot SO_2$, melting at −84°C, which may be fluorosulfinic acid, $HO\underset{F}{S}O$. It is not at all certain that the substance has this structure (*273*).

2. *Salts of Fluorosulfinic Acid*

Fluorosulfinates of the alkali metals, other than lithium, and of the tetramethyl ammonium radical are made, according to Seel and Riehl (1955), by allowing sulfur dioxide (liquid or gaseous) to combine with fluorides of the alkali metals or with $(CH_3)_4NF$ (*273*). The larger the cation, the more rapidly the reaction occurs. The salts contain the SO_2F^- ion. As one might expect, KSO_2F is structurally similar to $KClO_3$.

Potassium fluorosulfinate reacts with the chlorides SO_2Cl_2, $SOCl_2$, $C_6H_5SO_2Cl$, PCl_3, $POCl_3$, $AsCl_3$, $ClCH_2COCl$, and C_6H_5COCl to give the corresponding fluorides. The potassium salt is a more convenient fluorinating agent than SbF_3, F_2, or HF. The preparation of thionyl fluoride may be accomplished, for example, by passing a stream of thionyl chloride vapor in nitrogen over a bed of potassium fluorosulfinate in a glass tube at 150°. Other reactions of fluorosulfinates are (*273*):

$$4MSO_2F + H_2O\ (g) = 2MHF_2 + M_2S_2O_5 + 2SO_2$$

$$2MSO_2F + 2H_2O\ (l) = MHSO_3 + MHF_2 + H_2SO_3$$

$$(CH_3)_4NSO_2F + MI \overset{\text{liq. } SO_2}{=} MSO_2F\ (s) + (CH_3)_4NI$$

$$2MSO_2F + SO_2 \overset{175°}{=} 2MSO_3F + S$$

$$MSO_2F + F_2 = SO_2F_2 + MF$$

$$MSO_2F + Cl_2 = SO_2ClF + MCl$$

V. Other Inorganic Compounds Containing Sulfur and Fluorine

A. Compounds Containing Phosphorus, Sulfur, and Fluorine

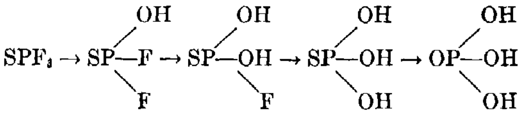
1. *Phosphorus Thiofluoride*, PSF_3

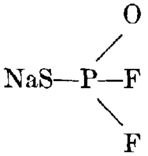
Thorpe and Rodgers (*299*) (1888) produced phosphorus thiofluoride by heating a mixture of PbF_2 and P_2S_5 or a mixture of PbF_2, S, and P. They also used the reaction

$$PSCl_3 + AsF_3 \xrightarrow[150^\circ]{} PSF_3 + AsCl_3.$$

Others have used modifications of the first of the above procedures (*183*, *313*). The Swarts reaction involving $PSCl_3$ or $PSBr_3$ and SbF_3 has also been used (*18*, *22*).

PSF_3 is a colorless gas which burns in air. The products are said to be PF_3, SO_2, and, probably, POF_3 (*299*). Another author gives PF_5, P_2O_5, and SO_2 as the products (*211*). Phosphorus thiofluoride reacts slowly with water and more rapidly with a solution of sodium hydroxide (*183*, *299*). The hydrolysis goes by steps giving HF and H_2S (or F^- and $S^=$ or HS^-) and phosphoric acids (or their anions) such as those shown in the hydrolysis scheme proposed by Lange and Askitopoulos (*183*),



By the reaction with cold NaOH Solution Lange has obtained the salt  (*182*). Ammonia reacts with phosphorus thiofluoride to give $(NH_2)_2PSF$, a white solid (*183*, *299*) that hydrolyzes in moist air to form $[PS(NH_2)_2]OH$ (*211*). PSF_3 attacks some metals (*313*) and hot glass (*299*).

The vapor pressure of PSF_3 is given by the equation

$$\log_{10} P_{\text{mm}} = 7.5882 - 1038.8/T.$$

This gives a heat of vaporization of 4684 kcal/mole. The critical temperature is 72.8° and the critical pressure is 37.7 atm (*18*).

Electron diffraction (*290*) gives a structure having the parameters: $r_{PF} = 1.51 \pm 0.02$ Å, $r_{PS} = 1.85 \pm 0.02$ Å, $\angle FPF = 99.5 \pm 2^\circ$, $\angle FPS = 118 \pm 2^\circ$. From the microwave spectrum (*131*, *322*) the parameters are: $r_{PS} = 1.87 \pm 0.03$ Å, $r_{PF} = 1.53 \pm 0.02$ Å, $\angle FPF = 100.3 \pm 2^\circ$.

Some thermodynamic properties have been calculated from the infrared spectrum (*336*).

2. Phosphorus Thiochlorofluorides

Booth and Cassidy (1940) produced $PSClF_2$ and $PSCl_2F$ by the reaction of $PSCl_3$ with a mixture of antimony trifluoride and antimony pentachloride at about 75° (*18*). These compounds hydrolyze in moist air and react rather slowly with potassium hydroxide solution. They do not ignite spontaneously in air as readily as does PSF_3; however, a mixture with air is spontaneously explosive (*18*).

Equations for the vapor pressures are:

$$\log_{10} P_{\mathrm{mm}} = 7.5100 - 1292.7/T \text{ (for } PSClF_2\text{)}$$
$$\log_{10} P_{\mathrm{mm}} = 7.6596 - 1613.9/T \text{ (for } PSCl_2F\text{)}$$

The heats of vaporization per mole are 5703 cal and 6863 cal for $PSClF_2$ and $PSCl_2F$, respectively. Phosphorus thiochlorodifluoride has a critical temperature of 166.0° and a critical pressure of 40.9 atm.

3. Phosphorus Thiobromofluorides

Booth and Seabright (1943, *22*) produced $PSBrF_2$ and $PSBr_2F$ by the reaction of $PSBr_3$ with SbF_3 at about 65°. By the same sort of reaction Delwaulle and Francois (*65*) have prepared PSClBrF from $PSClBr_2$. These compounds hydrolyze slowly in basic solutions. They are not highly reactive in general but few chemical reactions are known (*22*).

Structures for two of these compounds are known to resemble that of PSF_3. The parameters as determined by electron diffraction (*32*) are: for $PSBr_2F$, $r_{\mathrm{PS}} = 1.87 \pm 0.05$ Å, $r_{\mathrm{PF}} = 1.50 \pm 0.10$ Å, $r_{\mathrm{PBr}} = 2.18 \pm 0.13$ Å, $\angle \mathrm{BrPBr} = 100 \pm 3°$; for $PSBrF_2$, $r_{\mathrm{PS}} = 1.87 \pm 0.04$ Å, $r_{\mathrm{PF}} = 1.45 \pm 0.08$ Å, $r_{\mathrm{PBr}} = 2.14 \pm 0.05$ Å, $\angle \mathrm{FPBr} = 106 \pm 3°$. Equations for the vapor pressures of the same two compounds are:

$$\log_{10} P_{\mathrm{mm}} = 7.4674 - 1827.3/T \text{ (for } PSBr_2F \text{ up to 760 mm)}$$
$$\log_{10} P_{\mathrm{mm}} = 7.6970 - 1484.8/T \text{ (for } PSBrF_2 \text{ up to 760 mm)}$$

The heats of vaporization per mole are 8351 and 6775 cal for $PSBr_2F$ and $PSBrF_2$, respectively (*22*).

4. Phosphorus Difluoroisothiocyanate, PF_2NCS

In 1947 Anderson (*3*) reported the preparation of PF_2NCS by the reaction of $P(NCS)_3$ with SbF_3 at about 175°. An equation for the vapor pressure is $\log_{10} P_{\mathrm{mm}} = 7.7045 - 1752.9/T$ and the heat of vaporization is 8080 cal/mole. The compound is completely miscible with carbon disulfide and its stability is "fairly high" (*3*).

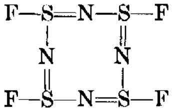
5. *Diethyl Fluorothiophosphate,* $(C_2H_5O)_2\overset{S}{P}F$

White (1952, *319*) produced the ester, $(C_2H_5O)_2\overset{S}{P}F$, by warming together hydrogen fluoride and $(C_2H_5O)_2\overset{S}{P}O\overset{S}{P}(OC_2H_5)_2$. The product is soluble in ethanol, acetone, and ether. It is slightly soluble in water and it hydrolyzes but does not attack glass. The odor is nauseating but the toxicity is not particularly high.

B. COMPOUNDS OF SULFUR, NITROGEN, AND FLUORINE

$S_4N_4F_4$ is prepared (Glemser *et al.*, 1955, *109*, *110*) by adding AgF_2 to a solution of S_4N_4 in carbon tetrachloride and then warming the mixture to a temperature near its boiling point for about 15 minutes. This process gives a red solution from which white crystals of $S_4N_4F_4$ may be separated as the solvent is removed. Upon being warmed, the compound starts to decompose at about 128° and it becomes completely molten at 153°. Its solubility in carbon tetrachloride at 20° is 3.44 gm/liter. An X-ray study of the solid indicates a tetragonal structure and a space group of $P\bar{4}21c{-}D_{2d}^{4}$ with $a = 9.2$ Å and $c = 4.3$ Å. The unit cell contains two formula weights of $S_4N_4F_4$. A molecule has a dipole moment of 0.

The compound hydrolyzes slowly in moist air. With warm NaOH solution it gives NH_4OH, F^- and $SO_3^=$. This indicates an oxidation number of +4 for sulfur. All of the above properties are in accord with the proposed structure



SN_2F_2 is a colorless gas formed by refluxing a solution of S_4N_4 in carbon tetrachloride with AgF_2 for a period of about two hours (*109*, *110*). The gas reacts rapidly with warm sodium hydroxide solution forming NH_4OH, F^-, and $SO_3^=$. It also reacts with mercury and stopcock grease. Vapor pressures at a few temperatures are:

Vapor pressure (mm of Hg)	16.0	141.6	281.9	445.4	668.9
Temperature (°K)	191	226	239	249	259

The proposed structure is $F{-}N{=}\overset{+}{S}{-}\overset{-}{N}{-}F$ (*109, 110*). At its boiling point SN_2F_2 decomposes into N_2, NSF, SNF_3, and another colorless liquid compound of S, N, and F melting at ∼20° and boiling at ∼60° (*108*).

SNF in an impure form presumably containing SN_2F_2 has been obtained by the fractional distillation of crude SN_2F_2 (*109, 110*). The composition of the molecule has been learned by analyzing (for S and F) and measuring the densities of several samples of the impure material. Hydrolysis in NaOH solution gives NH_4OH, F^-, $SO_3^=$, and $S^=$. As the impure gas stands for a long time, green-gold crystals of solid $S_xN_yF_z$ collect on the walls of the glass container. The proposed structure of SNF is S=N—F.

SNF_3 is obtained by passing a gaseous mixture of SNF and SN_2F_2 over AgF_2 at about 20°. (Glemser and Schröder 1956, *111*). The thermal decomposition of SN_2F_2 at its boiling point proceeds slowly and forms N_2, SNF_3, NSF, and a colorless liquid (mp ∼−20°, bp ∼60°) which contains the elements N, S, and F (*108*). The compound SNF_3 is a colorless gas which is hydrolyzed by water. With NaOH solution it gives NH_4OH, F^-, and $SO_3^=$. A heat of vaporization for the liquid of 5210 cal/mole is found from vapor pressure measurements. The proposed structure is $F_2S{=}NF$.

NSF is formed along with SiF_4 and N_2 when SN_2F_2 is decomposed in a quartz glass vessel at 250° (*108*). This compound is considered to be an isomer of SNF and to have a structure N=S—F. It is isoelectronic with SO_2 to which it bears a physical resemblance. The gas is colorless and it reacts with NaOH solution to give NH_4OH, F^-, and $SO_3^=$. By hydrolysis the isomer, SNF, gives NH_4OH, F^-, $SO_3^=$ and $S^=$. A few vapor pressures are:

Vapor pressure (mm of Hg)	21	59	104	158	258	645
Temperature (°K)	213.2	220.9	230.7	239.3	250.5	273.2

The heat of vaporization is 5300 cal/mole.

C. COMPOUNDS CONTAINING SULFUR, ANTIMONY, AND FLUORINE

$(SbF_5)_2S$ is obtained (Aynsley *et al.*, *4a*) by the reaction of sulfur with antimony pentafluoride. It is a white solid and is stable up to about 200°. The related compounds $(SbF_5)Se$ and $(SbF_5)_5Te$ are also known.

$SbF_5 \cdot SO_2$ is formed by combining antimony pentafluoride with sulfur dioxide (*4a*). It is a white solid which melts at 57° to a mobile colorless liquid. It reacts rapidly with water forming sulfur dioxide. Arsenic pentafluoride does not combine with sulfur dioxide.

D. SULFUR CONTAINING COMPOUNDS FORMED BY THE ADDITION OF BF_3

1. Compounds in Which BF_3 *Is Loosely Bound*

Studies by H. S. Booth and co-workers of the freezing points for systems involving boron trifluoride have shown the existence at low temperatures of solid compounds of low stability. They decompose easily to give BF_3 and the other components. The compounds which contain sulfur are given in the tabulation.

Formula	$BF_3 \cdot H_2S$	$BF_3 \cdot 7H_2S$	$BF_3 \cdot SOF_2$	$BF_3 \cdot SO_2$
mp (°C)	−137	−99	−140.8	−96
Reference	*106*	*106*	*23*	*20*

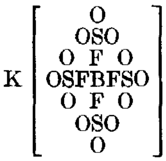
2. $SF_4 \cdot BF_3$ *(6, 56)*

This compound is discussed in Section II.C.

3. Boron Trifluoride and Sulfates

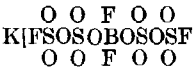
Baumgarten and Müller (1936, *10*), also Baumgarten and Hennig (1939, *9*), found that boron trifluoride combines with certain sulfates at about 250–300° to form the compounds $Na_2SO_4 \cdot BF_3$, $K_2SO_4 \cdot BF_3$, $Cs_2SO_4 \cdot 2BF_3$, and $Tl_2SO_4 \cdot BF_3$. The potassium salt becomes completely molten when heated to 240° and at about 260° it decomposes. The salts are white crystalline solids at room temperature.

A related compound, $KBF_4 \cdot 4SO_3$ (Baumgarten, 1940) is formed by adding sulfur trioxide in excess to potassium fluoroborate at 45–70°. After removal of the excess SO_3 white crystalline $KBF_4 \cdot 4SO_3$ remains (*8*). When this solid is heated, it begins to decompose at about 65° forming SO_3 and $S_3O_8F_2$ which distil away (*186*). Proposed structures are



$$K\left[\begin{array}{c} O \\ OSO \\ O\ F\ O \\ OSFBFSO \\ O\ F\ O \\ OSO \\ O \end{array}\right]$$

(*8*) and



$$K[\begin{array}{c} O\ O\ F\ O\ O \\ FSOSOBOSOSF \\ O\ O\ F\ O\ O \end{array}]$$

(*186*).

E. THE COMPOUND $SCl_4 \cdot 2AsF_3$

Sulfur tetrachloride and arsenic trifluoride combine readily to form $SCl_4 \cdot 2AsF_3$ (Ruff and Thiel, 1904, *251*). The substance is a pale yellow solid which is very hygroscopic. It hydrolyzes rapidly in water or NaOH solution and attacks organic matter. Glass is attacked only slowly.

VI. Compounds Containing Carbon, Sulfur, Fluorine, and Elements other than Oxygen

A. COMPOUNDS WITH FLUORINE BOUND TO CARBON BUT NOT TO SULFUR

1. *Thiocarbonyl Fluoride*, CSF_2

The literature regarding thiocarbonyl fluoride, CSF_2, is confusing. It is doubtful whether the pure compound has been isolated; consequently, its existence is not certain. There is a report (*30*) that the compound was prepared by O. Ruff using the reaction of IF_5 with CS_2 and that it melted at −136° and boiled at −40°. When the same reaction was tried by Haszeldine and Kidd (1953, *138*) no CSF_2 was found as a product, but the use of partially hydrolyzed IF_5 caused the formation of SOF_2, a substance having properties like those reported for CSF_2. Bennett *et al.* (1950, *13*) and Brandt *et al.* (*27*) reported CSF_2 to be formed by heating sulfur with CF_3I, but further work by Haszeldine and Kidd (*138*) with the same reaction was not reported to give thiocarbonyl fluoride. Still later (1955) Haszeldine and Kidd (*141*) said that they obtained a product thought to be impure CSF_2 by the reaction of CF_3SH with NaF at room temperature. The product was not formed by the same reactants at 55°, but it was assumed to be an intermediate product of the hydrolysis of CF_3SH (*141*). In 1953 Tyczkowski and Bigelow (*310*) described an impure sample of a material considered to be thiocarbonyl fluoride. It was a small part of the product resulting from the action of fluorine upon carbon disulfide and it had a boiling point of −46° and melting point of −134°. The authors expressed uncertainty about the formula for the compound.

2. *Trifluoromethanethiol*, CF_3SH

The compound CF_3OH has not been prepared. Instead, one obtains COF_2 and HF.

Hydrogen chloride reacts with $(CF_3S)_2Hg$ to form mercuric chloride and CF_3SH (*138*). The compound reacts with NaOH solution to give $CO_3^{=}$ F^-, and $S^{=}$ ions. Under prolonged irradiation by ultraviolet light it decomposes into H_2, CHF_3, $(CF_3)_2S$, $(CF_3S)_2$, and S (*138*). As CF_3SH reacts with an excess of water, a yellow liquid ($CF_3S\overset{S}{C}F$) is formed at first. Carbonyl sulfide is also produced. With a little water in a glass vessel the products include COS, SiF_4, and, perhaps, CSF_2. At room temperature sodium fluoride and CF_3SH react in glass to form $CF_3S\overset{S}{C}F$, COS, SiF_4, and, perhaps, CSF_2. The latter is not obtained at 55°. Equal numbers of moles of CF_3SH and anhydrous NH_3 react in a glass vessel to give $CF_3\overset{S}{C}F$, COS, SiF_4, $(CF_3S)_2CS$, NH_4F, $CF_3S\underset{S}{C}NH_2$?, and, perhaps, CSF_2 (*138*).

3. Other R_fSH *Compounds*

Known compounds of this type are C_3F_7SH (*141*) and $H(CF_2CF_2)_3CH_2SH$ (*94*).

4. Trifluoromethanesulfenyl Chloride, CF_3SCl

When $(CF_3S)_2Hg$ reacts with chlorine in a glass tube at about −20° the products obtained are: $HgCl_2$, CF_3SHgCl, $(CF_3S)_2$, and CF_3SCl (Haszeldine and Kidd, 1953, *138*). When the temperature of the reaction is increased to 20° the yield of CF_3SCl is reduced. Under the influence of ultraviolet light $(CF_3S)_2$ reacts with Cl_2 to form CF_3SCl. Trifluoromethanesulfenyl chloride reacts with NaOH solution. With mercury it gives $HgCl_2$ and $(CF_3S)_2$. With CF_3SH it slowly gives HCl and $(CF_3S)_2$. There is a slow reaction with H_2S which forms CF_3SSSCF_3. The compound CF_3SCl has a golden yellow color and vapor pressures as shown:

Vapor pressure (mm of Hg)	262.2	316.0	446.6	740.3	760.0
Temperature (°C)	−25.1	−21.3	−13.7	−1.3	−0.7

5. Other R_fSCl *Compounds*

Knunyants and Fokin (1955, *171*) have prepared $ClCF_2CF_2SCl$ by combining S_2Cl_2 or SCl_2 with C_2F_4 at about 110° and by the reaction of Cl_2 with $(ClCF_2CF_2S)_2$ at 100°. Several chemical and physical properties are known. The reaction of SCl_2 with C_2F_4 produces both $ClCF_2CF_2SCl$ and $ClCF_2CF_2SSCl$ for which physical constants are known (*171*).

The compound $ClCF_2CH_2SCl$ is formed when chlorine reacts with $(ClCF_2CH_2S)_2$ (*169*). Physical constants of $ClCF_2CH_2SCl$ are known as are several of its chemical reactions and the nature of the compounds formed by the reactions (*169*). For example, $ClCF_2CH_2SCl$ reacts with $(C_2H_5)_2NH$ in $(C_2H_5)_2O$ to form $ClCF_2CH_2SN(C_2H_5)_2$.

6. Bis(trifluoromethyl) sulfide, $(CF_3)_2S$

The ultraviolet irradiation of $(CF_3S)_2$ in a silica tube produces sulfur and bis(trifluoromethyl) sulfide (Brandt *et al.*, 1952, *26*). It is also obtained by the irradiation of $(CF_3S)_2S$ (*138*) and by the thermal decomposition of

$(CF_3S)_2$ or $(CF_3S)_2Hg$ (*141*). The compound strongly resists hydrolysis by NaOH solution being scarcely, if at all, attacked even at 150°C. Its vapor pressure follows the equation

$$\log_{10} P_{\mathrm{mm}} = 7.816 - 1239.1/T$$

This corresponds to a heat of vaporization of 5650 cal/mole (*26*). Structural parameters obtained by electron diffraction are (*24*): $r_{CF} = 1.328 \pm 0.001$ Å, $r_{CS} = 1.828 \pm 0.015$ Å, $\angle CSC = 105.6 \pm 3°$.

7. *Other* R₂S *Compounds Containing* F *Atoms in the Radicals*

Among the products of reaction of C_3F_7I with sulfur is a small yield of a material, bp about 90°, thought probably to be $(C_3F_7)_2S$ (Hauptschein and Grosse, 1951, *130*). A similar reaction produces $[H(CF_2)_6CH_2]_2S$ (*94*). An olefin such as C_2F_4, C_2ClF_3, C_2BrF_3, C_2F_3I reacts with SCl_2 or S_2Cl_2 under pressure at about 100–150° to give sulfides, disulfides, and trisulfides (Raasch, 1948, *245*; Knunyants and co-workers, 1955, *169*, *171*) including $(CF_2ClCF_2)_2S$. Compounds of the type R_2S are also prepared by the reaction of an olefin such as $CH_2{=}CF_2$ with a sulfenyl chloride such as $ClCF_2CH_2SCl$ (*169*, *171*). By this means the compounds $(ClCF_2CH_2)_2S$, $ClCF_2CH_2SC_6H_{10}Cl$, $ClCF_2CH_2SC_2H_5$, $ClCH_2CH_2SCH_2CF_2Cl$, and others have been produced. Some of their chemical and physical properties are known (*169*). The compound $ClCF_2CH_2SCl$ reacts with C_6H_5MgBr to give $ClCF_2CH_2SC_6H_5$, and $ClCF_2CH_2Br$ reacts with Na and C_2H_5SH in methanol to form $C_2H_5SCF_2CH_2Br$ (*169*). Still another method for making R_2S-type compounds is the reaction of RSH with an olefin in the presence of an alkali (*170*, *172*). Compounds of the type R_1SR_2 are known in which R_1 is CH_3, C_2H_5, $i\text{-}C_3H_7$, or C_6H_5, and R_2 is $—CF_2CFClH$, $—CFClCFClH$, or $—CF_2CF_2H$. The compounds $CH_3SCF{=}CFCl$ and $C_2H_5SCF{=}CFCl$ and $CF_3CHFCF_2SCH_3$ are also known (*170*, *172*).

Another method for preparing R_1SR_2 compounds is by the reaction of SbF_3 and $SbCl_5$ with a sulfide containing chlorine (*308*). For example, CH_3SCCl_3 is converted to CH_3SCF_3. Other compounds produced in this way are CF_3SCH_2Cl, CF_2ClSCH_2Cl, CF_3SCF_2H, and CH_3SCF_2Cl. Some of their physical constants are known.

8. *Bis(trifluoromethyl) polysulfides*, CF_3SSCF_3, CF_3SSSCF_3, $CF_3SSSSCF_3$

The reaction of CF_3I with sulfur at about 260° produces CF_3SSCF_3, bis(trifluoromethyl) disulfide (Bennett *et al.*, *13*, *26*, *85*). This same reaction at about 300° also produces small yields of CF_3SSSCF_3, bis(trifluoromethyl) trisulfide, and $CF_3SSSSCF_3$, bis(trifluoromethyl) tetrasulfide (Haszeldine and Kidd, 1953, *138*). Both the disulfide and the trisulfide are also formed by the reaction of IF_5 with CS_2 at 195° (*138*). Other reactions which produce $(CF_3S)_2$ are: (a) ultraviolet irradiation of CF_3SH, (b) reaction of Cl_2 with $(CF_3S)_2Hg$, (c) reaction of Hg with CF_3SCl, (d) reaction of CF_3SCl with CF_3SH, (e) ultraviolet irradiation of CF_3SCl, (f) hydrolysis of CF_3SCl (*138*, *140*), (g) reaction of mercuric fluoride with carbon disulfide at 250° or more (*220*). Bis(trifluoromethyl) trisulfide is formed as hydrogen sulfide reacts slowly with CF_3SCl (*138*).

These polysulfides are stable to air, water, and mercury at 20° but they react with warm NaOH solution (*138*). Thermal decomposition of $(CF_3S)_2$ at 320° gives CS_2, CF_4, and $(CF_3)_2S$ (*141*). Ultraviolet irradiation of CF_3SSSCF_3 gives S and CF_3SCF_3 (*138*). When irradiated with ultraviolet light, $(CF_3S)_2$ reacts with mercury to give $(CF_3S)_2Hg$ (*26*) and with chlorine to give CF_3SCl (*138*). At 360° chlorine and $(CF_3S)_2$ react in the dark to form CF_3Cl and S_2Cl_2. Cobalt trifluoride and $(CF_3S)_2$ produce CF_3SF_5 (*26*). The reaction of $(CF_3S)_2$ with concentrated sulfuric acid in glass at 120° gives S, SO_2, CO_2, and SiF_4 (*139*).

The vapor pressure of $(CF_3S)_2$ follows the equation:

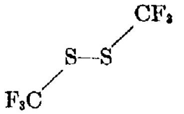
$$\log_{10} P_{\text{mm}} = 7.765 - 1506.1/T$$

From this the heat of vaporization is 6880 cal/mole (*26*).

Structural parameters found by electron diffraction are given in the tabulation.

	r_{CF}(Å)	r_{CS}(Å)	r_{SS}(Å)	∠CSS	∠SSS
$(CF_3S)_2$	1.334±0.013	1.829±0.017	2.053±0.019	105.4±3°	
$(CF_3S)_2S$	1.340± .011	1.848± .015	2.065± .016		103.8±3°

The $(CF_3S)_2$ molecule exists in the *trans* form (*24*).



9. *Other Polysulfides Containing* C—F *Groups*

C_3F_7I reacts with sulfur at about 250° forming $C_3F_7SSC_3F_7$, bis(perfluoro-*n*-propyl) disulfide, bp 122.2°, and $C_3F_7SSSC_3F_7$, bis(perfluoro-*n*-propyl) trisulfide, bp 153° (Hauptschein and Grosse, 1951, *130*). (For similar work see references *94* and *141*.) Disulfides are also produced by the reaction of SCl_2 or S_2Cl_2 at about 100–150° with olefins such as C_2F_4, C_2ClF_3, etc. (Raasch, 1948, *245*; Knunyants and co-workers, 1955, *169*, *171*). The known polysulfides which have been prepared by the latter method include $(ClCF_2CF_2S)_2S$, $(ClCF_2CF_2S)_2$, $(ClCF_2CH_2S)_2$, $(ClCF_2$-

$CH_2S)_2$, and $ClCF_2CF_2SSC_6H_{10}Cl$. Properties of some of these are known (*169*, *171*).

10. Trifluoromethylthiometal Compounds, $(CF_3S)_2Hg$, *etc.*

When trifluoromethyl disulfide $(CF_3S)_2$ is in contact with mercury and the mixture is irradiated by ultraviolet light, the two substances combine to form bis(trifluoromethylthio)mercury, $(CF_3S)_2Hg$ (Brandt *et al.*, *26*). Bis(heptafluoropropylthio)mercury, $(C_3F_7S)_2Hg$ has also been produced (*141*). The compound, $(CF_3S)_2Hg$, is also formed by the reaction of mercuric fluoride with carbon disulfide at about 250°. $(CF_3S)_2Hg$ melts at 37–38° (*220*).

When $(CF_3S)_2Hg$ and $AgNO_3$ react in aqueous solution trifluoromethylthiosilver, CF_3SAg is formed. A similar copper compound is made at 100–150° by heating a mixture of powdered copper with $(CF_3S)_2Hg$. Extraction with $(C_2H_5)_2O$ followed by evaporation of the solvent gives CF_3SCu. When this compound is recrystallized from CH_3CN the solid has the formula $CF_3Cu \cdot CH_3CN$ (*220*). At 50° $CSCl_2$ reacts slowly with $(CF_3S)_2Hg$ to form CF_3SHgCl, trifluoromethylthiomercuric chloride and $(CF_3)_2CS_3$. Pyrolysis in glass of $(CF_3S)_2Hg$ at 220° gives COS, CF_3SCF_3, CO_2, SiF_4, and perhaps, CSF_2 (*141*). The reaction of $(CF_3S)_2Hg$ with HCl at room temperature gives $HgCl_2$ and CF_3SH, and the reaction with Cl_2 at about −22° gives $(CF_3S)_2$, CF_3SCl, and $HgCl_2$ (*138*).

11. Bistrifluoromethyl Trithiocarbonate, $(CF_3S)_2CS$, *and Trifluoromethyl Fluorodithioformate,* $CF_3S\overset{S}{C}F$

When equal numbers of moles of NH_3 and CF_3SH are mixed in a glass vessel at −80° and the mixture is then allowed to warm to room temperature, the reaction which occurs produces $CF_3S\underset{S}{C}F$, $(CF_3S)_2CS$, COS, SiF_4, NH_4F, and, perhaps, $CF_3S\underset{S}{C}NH_2$ and CSF_2 (Haszeldine and Kidd, 1955).

The compound $(CF_3S)_2CS$ is also produced by the reaction of $CF_3S\overset{S}{C}F$ with $(CF_3S)_2Hg$ at 70°, and by the reaction of $(CF_3S)_2Hg$ with $CSCl_2$ at 50°.

$(CF_3S)_2CS$ is a red liquid which does not react with water at room temperature but does react at 80° giving COS as a product. It reacts with 15% NaOH at room temperature forming F^-, $S^=$, and other products.

$CF_3S\overset{S}{C}F$ is a yellow liquid which reacts with water at 75° forming CF_3SH, CO_2, and COS. With NaOH solution it gives F^-, $S^=$, and other products (*141*).

B. COMPOUNDS WITH FLUORINE BOUND TO SULFUR AND CARBON

1. Derivatives of Sulfur Tetrafluoride

Tyczkowski and Bigelow, 1953, obtained CF_3SF_3 (trifluoromethylsulfur trifluoride) and $F_3SCF_2SF_5$ together with CF_4, SF_6, SF_4, CF_3SF_5, S_2F_{10}, $SF_5CF_2SF_5$, and, perhaps, CSF_2 by the reaction at about 48° of carbon disulfide with fluorine highly diluted by nitrogen (*310*). CF_3SF_3 has also been formed by the reaction of $(CF_3)_2SF_4$ with $CF_3N{=}CF_2$ at about 520° (*73*).

CF_3SF_3 resembles SF_4 in its reactivity. It attacks glass slowly at room temperature and reacts with aqueous base (*73*).

The electrolysis of hydrogen fluoride containing carbon disulfide and a little sodium fluoride gives a gaseous product containing CF_3SF_5, $CF_2(SF_5)_2$, and $CF_2(SF_3)_2$, difluoromethylenebis(sulfur trifluoride (*51*).

2. Derivatives of Sulfur Hexafluoride

a. Trifluoromethylsulfur Pentafluoride, CF_3SF_5. The compound CF_3SF_5 (Silvey and Cady, 1950, *279*) is prepared by: (a) the electrolysis of hydrogen fluoride containing carbon disulfide (*51*, *280*) or dimethyl sulfide (*73*), (b) the reaction of cobalt trifluoride with carbon disulfide, methyl mercaptan (*279*), or bis(trifluoromethyl) disulfide (*26*), (c) the reaction of fluorine with methyl mercaptan in the presence of a porous mass of copper coated with fluorides of silver (*279*), (d) the reaction of fluorine with CS_2 (*310*). In the third process a compound of the empirical formula $CSHF_7$ is formed (*279*).

Trifluoromethylsulfur pentafluoride resembles sulfur hexafluoride by being an excellent gaseous electrical insulator (*104*, *105*, *123*, *124*) and by being highly resistant toward hydrolysis. Like sulfur hexafluoride it reacts with a hot alkali metal. It is more easily decomposed by a spark than SF_6 and the products are CF_4 and SF_4 (*279*). When the gas is passed through a nickel tube at 450° there is substantially no decomposition; at 500° there is a slow decomposition, or reaction with the nickel tube, to give C_2F_6 and SF_4. As a mixture of CF_3SF_5 and perfluoropropylene, C_3F_6, passes through a nickel tube at about 500–520° the reaction produces SF_4, C_2F_6, C_5F_{12} (three isomers), C_6F_{14}, and C_7F_{16} (*72*).

The compound $CSHF_7$ reacts readily with NaOH solution to give F^- and other products. It decomposes in a spark-over electrical discharge to give CF_4, CHF_3, and SF_4 (*279*).

For CF_3SF_5, the vapor pressure is given by the equation $\log_{10} P_{mm} = 6.71988 - 757.795/T - 53{,}771.9/T^2$; while the corresponding equation for $CSHF_7$ is $\log_{10} P_{mm} = 6.64570 - 759.863/T - 80{,}107.2/T^2$. The corresponding heats of vaporization per mole are 5,380 and 6,100 cal/mole (*279*). The moment of inertia (*167*) found from the microwave spectrum of CF_3SF_5 corresponds to the structural parameters: $r_{SF} = 1.57$ Å, $r_{CF} = 1.35$ Å, $r_{CS} = 1.86$ Å, $\angle FCF = 107° 30'$, $\angle FSF = 90°$.

b. Other R_fSF_5 *Compounds* (*73, 147*). The electrochemical process is used to produce $C_2F_5SF_5$ (bp, 135°), $C_3F_7SF_5$ (bp, 42°), $C_4F_9SF_5$ (bp, 68.7°), and $(C_2F_5)_2NCF_2CF_2SF_5$ (bp, 123°). Some properties of these compounds are known.

c. Difluoromethylenebis(sulfur pentafluoride), $F_5SCF_2SF_5$. A small yield of $F_5SCF_2SF_5$ results from the action of diluted fluorine upon carbon disulfide (Tyczkowski and Bigelow, 1953, *310*). The same substance is formed in small yield by the electrolysis of CS_2 in hydrogen fluoride containing sodium fluoride (Clifford *et al.*, *51*).

d. $SF_5CF_2SF_3$ (see Section VI.B.1).

e. Bis(trifluoromethyl)sulfur Tetrafluoride, $(CF_3)_2SF_4$ *and Other* $R_{f_2}SF_4$ *Compounds.* A compound of the formula $(CF_3)_2SF_4$ is one of the products obtained in small yield by the electrolysis of $(CH_3)_2S$ in hydrogen fluoride (*51, 73*). When a mixture of the compound with $CF_3N{=}CF_2$ is heated to 520° the reaction products include CF_4, C_2F_6, SF_4, and CF_3SF_3 (*73*). $(CF_3)_2SF_4$ reacts with $CF_3CF{=}CF_2$ at 518° to form SF_4, C_3F_8, and C_5F_{12} (mostly *neo*-C_5F_{12}) (*74*).

TABLE V

SYNTHESIS AND PROPERTIES OF $R_{f_2}SF_4$ COMPOUNDS

Organic solute in HF	$R_{f_2}SF_4$ compound of related structure	Boiling point (°C)	n_D^{25}	d^{25}	Reference
$(C_2H_5)_2S$	$(C_2F_5)_2SF_4$	70	1.2753	1.836	*73, 147*
$(C_3H_7)_2S$	$(C_3F_7)_2SF_4$	116	1.2856	1.865	*147*
$(C_4H_9)_2S$	$(C_4F_9)_2SF_4$	154	1.2943	1.903	*147*
$CH_2CH_2SCH_2CH_2$	$CF_2CF_2SF_4CF_2CF_2$	70	1.2766		*147*
$CH_2CH_2OCH_2CH_2S$	$CF_2CF_2OCF_2CF_2SF_4$	80	1.3015	1.859	*147*
$[(C_2H_5)_2NCH_2CH_2S]_2$	$(C_2F_5)_2NCF_2CF_2SF_5$	123	1.2921		*147*

The electrochemical process has also been used to obtain the derivatives of sulfur hexafluoride shown in Table V.

The nuclear magnetic resonance spectra of $R_{f_2}SF_4$ and of R_fSF_5 compounds indicate: (1) the fluorine nuclei of the R_f groups are more shielded by electrons than those of the $—SF_5$ and $=SF_4$ groups; (2) the $—SF_5$ groups have four identical fluorine atoms and one (presumably at the apex of a square pyramid) which is different; (3) in $R_{f_2}SF_4$ there is only one resonance peak for the $=SF_4$ fluorine atoms; therefore, the two R_f groups are attached at 180° from each other; (4) in $\overline{CF_2CF_2OCF_2CF_2S}F_4$ there are two sets of triplet peaks for the $=SF_4$ group; therefore, the angle $\angle$CSC is about 90° rather than 180° (*223*).

VII. Perfluoroalkanesulfonic Acids, Their Anhydrides, Salts, and Esters

A. TRIFLUOROMETHANESULFONIC ACID, CF_3SO_3H

The compound CF_3SO_3H was first reported by Haszeldine and Kidd in 1954 (*139*). It is produced by adding concentrated sulfuric acid to $Ba(CF_3SO_3)_2$, or some other salt of trifluoromethanesulfonic acid, and then distilling off CF_3SO_3H (*29, 36, 114, 139*). The procedures differ in the method for first obtaining the salt. The known methods are: (1) electrolysis of hydrogen fluoride containing CH_3SO_2F or CH_3SO_2Cl (*29, 36, 114*) to give CF_3SO_2F which is later caused to react with a base to give a salt such as $Ba(CF_3SO_3)_2$ or KCF_3SO_3, (2) reaction of hydrogen peroxide with $(CF_3S)_2Hg$ to give an acidic solution from which $Ba(CF_3SO_3)_2$ is obtained through neutralization by $BaCO_3$ (*139*), (3) reaction of a base with CF_3SO_2Cl (*140*).

Some properties of trifluoromethanesulfonic acid are like those of fluorosulfonic acid. For example, the boiling points are almost identical, 166° and 163°, respectively, and both are very strong acids when dissolved in water (*29, 116, 139*). The acid is stable up to at least 350° but at 650° it decomposes into SO_2F_2, COF_2, CHF_3, and CO_2. It is soluble in water, alcohols, ethers, and ketones (*116*). With water it gives the compound $CF_3SO_3H \cdot H_2O$ (*36, 116*) which can be distilled unchanged, its vapor pressure being 15 mm at 120°. It reacts with PCl_5 to form CF_3SO_2Cl (*29, 116*).

The anhydride of trifluoromethanesulfonic acid is prepared by the reaction of the acid with phosphorus pentoxide (*36, 116*) or phosphorus pentachloride (*29*). The anhydride is a good esterifying agent (*116*). It reacts with aniline in $(C_2H_5)_2O$ to give $CF_3SO_3H \cdot NH_2\phi$ and $CF_3SO_2NH\phi$ (*29*). Trifluoromethanesulfonamide, $CF_3SO_2NH_2$ (*29, 114*), melts at −119°.

B. ESTERS OF TRIFLUOROMETHANESULFONIC ACID

CF_3SO_3H and ethylene react at room temperature to form the ester $CF_3SO_3C_2H_5$ and a low polymer of C_2H_4 (*116*). The ethyl ester is also obtained by the reaction of the acid with ethanol. CF_3SO_3H combines with $(C_2H_5)_2O$ to give $[(C_2H_5)_2OH^+CF_3SO_3^-]$ which decomposes when heated forming $CF_3SO_3C_2H_5$ (*116*). A general method for preparing esters of perfluoroalkane sulfonic acids is to allow the silver salt to react with an alkyl iodide (*29, 114*).

Esters of perfluoroalkane sulfonic acids are alkylating agents. For example, $CF_3SO_3C_2H_5$ reacts with benzene to give $C_6H_5C_2H_5$ and $C_6H_4(C_2H_5)_2$ (*116*).

C. Salts of Trifluoromethanesulfonic Acid

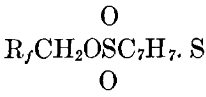
Methods for preparing salts have been given in Section VII.A. Salts which are known include $NaCF_3SO_3$ (mp, 248°) (*114*), KCF_3SO_3 (mp, 230°) (*29*), $AgCF_3SO_3$, and $Ba(CF_3SO_3)_2$ (mp above 370°) (*114*). The silver salt is soluble in benzene (*139*) and the barium salt is soluble in water, acetone, and alcohol. It does not act as a strong electrolyte in water (*139*).

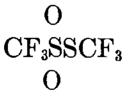
D. Other Perfluoroalkanesulfonic Acids and Derivatives

Numerous perfluoroalkane sulfonyl fluorides, R_fSO_2F, are prepared by the electrolysis of sulfonyl chlorides in liquid hydrogen fluoride. From these, the corresponding perfluoroalkanesulfonic acids are obtained by: (1) reaction of the sulfonyl fluoride with a base to give a salt, (2) distillation of the acid from a mixture of the salt with concentrated sulfuric acid (*29, 36, 115*).

These acids are much stronger and more stable than hydrocarbon sulfonic acids and perfluorocarboxylic acids. The higher acids are useful as surface active agents. The fluorocarbon chains of the higher acids are both hydrophobic and oleophobic. The potassium salts may be used as fusible fluxes, bonding agents and heat exchange liquids, or as high temperature lubricants (*29*). A few properties of known acids are: $C_2F_5SO_3H$, bp, 175 or 178°, surface tension at 25° = 21 dyne/cm, pyrolysis gives SO_2, CF_3COF, COF_2, $n\text{-}C_4F_{10}$ (*29, 115*); $C_5F_{11}SO_3H \cdot H_2O$, bp, 212°, mp, 129°; $C_6F_{13}SO_3H$, vapor pressure = 3.5 mm at 95°; $n\text{-}C_8F_{17}SO_3H$, bp, 249°; perfluoro-*p*-trifluoromethylcyclohexane sulfonic acid, bp, 240°, stable in water up to 250° (*29*); $C_8F_{17}SO_3H$, bp, 259° (*115*).

Anhydrides and salts of a few of the above acids are known (*29, 36, 115*).

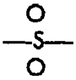
Alcohols of the type R_fCH_2OH react with *p*-toluenesulfonic acid to form esters of the type  $R_fCH_2O\overset{O}{\underset{O}{S}}C_7H_7$. Several esters of this kind are known (*94, 195, 300*)



E. Trifluoromethyl Trifluoromethanethiolsulfonate, $CF_3\overset{O}{\underset{O}{S}}SCF_3$

CF_3SCl reacts slowly with $Zn(CF_3SO_2)_2$ at room temperature to form $CF_3SO_2SCF_3$. The slow hydrolysis of CF_3SCl by the addition of successive small amounts of water produces both $(CF_3S)_2$ and $CF_3SO_2SCF_3$. Trifluoromethyl trifluoromethanethiolsulfonate is a colorless liquid which hydrolyzes in a basic solution to give CHF_3, F^-, $CO_3^=$, and $S^=$ or polysulfide ion (*140*).

VIII. Certain Compounds Containing the $-\overset{O}{\underset{O}{S}}-$ Bridge



A. SULFONYL FLUORIDES

1. *Perfluoroalkanesulfonyl Fluorides*

Trifluoromethanesulfonyl fluoride, CF_3SO_2F, is prepared by the electrolysis of CH_3SO_2Cl in hydrogen fluoride. The higher perfluoroalkanesulfonyl fluorides are prepared similarly. This application of the electrolytic process of Simons (*281*, *282*) was made independently by three parties: (a) Brice and Trott, 1956 (*29*); (b) Gramstad and Haszeldine, 1956 (*114*); (c) Burdon *et al.*, 1957 (*36*).

In these compounds the S-F bond is not very reactive. For example, CF_3SO_2F reacts only slowly with water and it does not react with C_2H_5OH at 100° (*114*, *116*) They react with bases to give salts of perfluoroalkanesulfonic acids (*29*, *36*, *114*). They are oxidized by NO_2 at high temperatures. For example, $C_8F_{17}SO_2F$ and NO_2 react at about 550° to give $C_7F_{15}COF$ and $NOSO_3F$ (*275*). A few reactions of CF_3SO_2F are (*114*, *116*):

$$CF_3SO_2F \xrightarrow{(C_2H_5)_2NH} CF_3SO_2N(C_2H_5)_2$$

$$CF_3SO_2F \xrightarrow{NH_3} CF_3SO_2NH_2$$

$$CF_3SO_2F \xrightarrow{C_2H_5ONa} CF_3SO_3Na + (C_2H_5)_2O$$

$$CF_3SO_2F \xrightarrow[(C_2H_5)_2O]{CH_3MgI} CF_3SO_2CH_3 + CF_3SO_2CH_2SO_2CF_3$$

Sodium borohydride reacts with $C_8F_{17}SO_2F$ in ether and alcohol at 16° to give perfluoro-*n*-octanesulfinate ion, $C_8F_{17}SO_2^-$. The *S*-benzylthiuronium salt of this ion melts at 130° (*36*).

Known perfluoroalkanesulfonyl fluorides include (*29*, *115*):

$C_2F_5SO_2F$; bp, 7.5°
$C_3F_7SO_2F$; bp, 36°
$C_4F_9SO_2F$; bp, 64°
$C_5F_{11}SO_2F$; bp, 90°, n_D^{25}, 1.2881
$C_6F_{13}SO_2F$; bp, 115°; n_D^{25}, 1.2918
$C_7F_{15}SO_2F$; bp, 135°; n_D^{25}, 1.297

n-$C_8F_{17}SO_2F$; bp, 155°; n_D^{25}, 1.2993

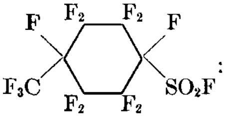
n-$C_{10}F_{21}SO_2F$; bp, 190°

n-$C_{12}F_{25}SO_2F$; bp, 222°

n-$C_{14}F_{29}SO_2F$; bp, 250°

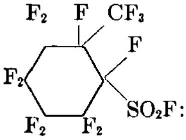
n-$C_{16}F_{33}SO_2F$; bp, 275°

n-$C_{18}F_{37}SO_2F$; bp, 295°

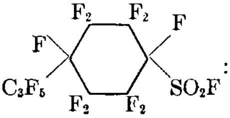


: bp, 131.5; n_D^{25} 1.318

cyclo-$C_6F_{11}SO_2F$: bp, 103°



: bp, 131°; n_D^{25} 1.318



: bp, 151°; n_D^{25} 1.321.

2. Other Sulfonyl Fluorides, RSO_2F

In 1927 Steinkopf reported the preparation of several aromatic sulfonyl fluorides (*287*). For example, he obtained benzene sulfonyl fluoride, $C_6H_5SO_2F$, by the slow addition of fluorosulfonic acid to benzene at about 20°. The crude product was poured over ice and was then extracted in ether. After evaporating the ether, the benzene sulfonyl fluoride was refined by steam distillation. Another method for preparing aromatic sulfonyl fluorides is by the reaction of an aromatic sulfonic acid, such as $C_6H_5SO_3H$, with fluorosulfonic acid (*202*). By boiling a mixture of an aromatic sulfonyl chloride with a concentrated solution of potassium fluoride in water, the chloride is converted to a fluoride (*62*).

Methanesulfonyl fluoride, CH_3SO_2F, and other alkanesulfonyl fluorides were prepared by Davies and Dick, 1932, by refluxing CH_3SO_2Cl over solid ZnF_2 or by heating an alkanesulfonyl chloride with 70% KF solution in water (*63*).

Methanesulfonyl fluoride boils at 124° (*63, 114*). It is hydrolyzed slowly by boiling water and more rapidly by NaOH solution giving F^- and the sulfonate (*63*). Benzenesulfonyl fluoride boils at 203° and reacts with: (a) NH_4OH to give ϕSO_2NH_2, (b) aniline to give $\phi SO_2NH\phi$, (c) ROH to give ϕSO_3R (*287*).

TABLE VI

PHYSICAL PROPERTIES OF VOLATILE FLUORINE-CONTAINING COMPOUNDS OF SULFUR

Formula	Name	bp (°C)	Trouton constant	mp (°C)	Density at °C (gm/ml)	n_D at °C	Reference	References to ir = infrared uv = ultraviolet Ra = Raman
				Fluorides of sulfur				
S_2F_2?	Disulfur difluoride	?		?			*47, 253, 306*	ir *82, 199*
SF_2?	Sulfur difluoride	−35?					*253*	ir *82*
SF_4	Sulfur tetrafluoride	−38 to −40	27.1	−121	1.9191	−73	*34, 74, 96, 138, 310*	ir *70;* Ra *70*
SF_6	Sulfur hexafluoride	−63.6 sub.		−50.8	1.912 2.515	(l) −50 (s) −50	*168, 242, 270, 271*	ir *83, 89, 102, 176, 177;* Ra *89, 329;* uv *295*
S_2F_{10}	Disulfur decafluoride	29.25	23.0	−54.2	2.08	0	*67, 155*	ir *83, 84*
				Oxyfluorides of sulfur				
SOF_2	Thionyl fluoride	−43.8	22.6	−129.5			*21, 207, 217, 253*	ir *233;* Ra *12, 329*
SO_2F_2	Sulfuryl fluoride	−52?		−120?			*11, 78, 217, 306*	ir *238;* Ra *12*
SOF_4	Thionyl tetrafluoride	−49		−99.6	1.808	−57	*78, 165, 174*	ir *78*
SF_5OF	Pentafluorosulfur hypofluorite	−35.1		−86.0	1.947	−47	*78*	ir *78*
SO_3F_2	Fluorine fluorosulfonate	−31.3	22.1	−158.5	1.784	−74	*76*	ir *76*
FO_2SOSO_2F	Pyrosulfuryl fluoride	51.0	23.5	−48	1.75	20	*50, 132, 135, 136*	ir *50*
FO_2SOOSO_2F	Peroxydisulfuryl difluoride	67.1	22.4	−55.4	1.645	35.5	*77, 314*	ir *77*
$S_2O_5F_4$	Monoperoxytetrafluorodisulfur(VI) oxide	~35 dec.		−95			*314*	
F_5SOOSF_5	Bis(pentafluorosulfur) peroxide	49		−95	1.82	20	*128*	

$S_3O_8F_2$	Trisulfuryl fluoride	120.0			1.86	25			*186*	
$SOClF$	Thionyl chlorofluoride	12.2	20.7	−139.5	1.576	0			*21, 165*	
SO_2ClF	Sulfuryl chlorofluoride	7.1	22.5	−124.7	1.623	0			*19*	
SO_2BrF	Sulfuryl bromofluoride	40.0		−86.0	2.12	21			*165*	
FO_2SOSO_2Cl	Pyrosulfuryl chlorofluoride	100.1	21.6	−65	1.797	20			*87*	
	Fluorosulfonic acid and its esters									
HSO_3F	Fluorosulfonic acid	162.6		−87.3	1.740	18			*298, 211, 209*	
$2AsF_3 \cdot 3SO_3$		141.9							*88, 221*	
CH_3SO_3F	Methyl fluorosulfonate	92			1.427	16			*209*	
$C_6H_5SO_3F$	Phenyl fluorosulfonate	180							*180, 184*	
	Other esters of HSO_3F								*41, 184, 209, 246*	
	Phosphorus thiofluoride, etc.									
PSF_3	Phosphorus thiofluoride	−52.3	21.2	−148.8					*18, 183, 313*	ir *336*
$PSClF_2$	Phosphorus thiochlorodifluoride	6.3	20.4	−155.2	1.484	0			*18*	
$PSCl_2F$	Phosphorus thiodichlorofluoride	64.7	20.3	−96.0	1.590	0			*18*	
$PSBrF_2$	Phosphorus thiobromodifluoride	35.5	22.0	−136.9	1.940	0			*22*	
$PSBr_2F$	Phosphorus thiodibromofluoride	125.3	21.0	−75.2	2.390	0			*22*	
$PSBrClF$	Phosphorus thiobromochlorofluoride	98			1.96				*65*	Ra *65*
PF_2NCS	Phosphorus difluoroisothiocyanate	90.3	22.2	−95	1.452	20	1.4978	20	*3*	
$PSF(OC_2H_5)_2$	Diethyl thiofluorophosphate	166					1.4188	25	*319*	

TABLE VI (*Continued*)

Formula	Name	bp (°C)	Trouton constant	mp (°C)	Density at °C (gm/ml)	n_D at °C	Reference	References to ir = infrared uv = ultraviolet Ra = Raman
Compounds of sulfur, nitrogen, and fluorine								
SNF							*110*	
NSF		4.8	19.1	−79	1.38 −60		*108*	
SNF_3		−23	20.8	−81	1.92 −80		*111*	
SN_2F_2		−11	20.7	−108	1.57 −80		*110*	
$S_4N_4F_4$				153(d)	2.326 20		*109*	
Compounds with fluorine bound to carbon but not to sulfur; oxygen absent								
CSF_2?	Thiocarbonyl fluoride	?−46, −40?		−134?			*13, 141, 173, 310*	
CF_3SH	Trifluoromethanethiol	−36.7					*138*	uv *138*
CF_3SCl	Trifluoromethanesulfenyl chloride	−0.7				yellow	*138*	uv *138*
$(CF_3)_2S$	Bis(trifluoromethyl) sulfide	−22.2	22.5				*26*	ir *27;* uv *138*
$(CF_3)_2S_2$	Bis(trifluoromethyl)disulfide	34.6	22.4				*13, 26, 138*	ir, uv, *27, 138*
$(CF_3)_2S_3$	Bis(trifluoromethyl)trisulfide	86.4				1.4023 20	*138*	uv *138*
$(CF_3)_2S_4$	Bis(trifluoromethyl)-tetrasulfide	135				1.4608 20	*138*	uv *138*
$(CF_3)_2CS_3$	Bis(trifluoromethyl) thiocarbonate	110				red	*141*	ir, uv, *141*
CF_3SCSF	Trifluoromethyl fluorodithioformate	43.9				yellow	*141*	ir, uv, *141*
Compounds with fluorine bound to carbon and sulfur; oxygen absent								
CF_3SF_3	Trifluoromethylsulfur trifluoride	−7		−110			*73, 310*	

$CF_2(SF_3)_2$	Difluoromethylenebis-(sulfur trifluoride)	35							*51*	
$F_3SCF_2SF_5$		26		−51					*310*	
CF_3SF_5	Trifluoromethylsulfur pentafluoride	−20.4	21.3	−86.9					*51, 72, 73* *279*	ir *51*; uv *51*
$CF_2(SF_5)_2$	Difluoromethylenebis-(sulfur pentafluoride)	60.5		−70					*51, 310*	ir, uv *51*
$(CF_3)_2SF_4$	Bis(trifluoromethyl)-sulfur tetrafluoride	20.5							*51*	ir *51*

Trifluoromethanesulfonic acid and derivatives

CF_3SO_3H	Trifluoromethanesulfonic acid	166, 162							*29, 116, 139*	ir *139*
$CF_3SO_3H \cdot H_2O$	Hydronium trifluoromethanesulfonate	120 at 15 mm		45 34					*36, 116*	ir *116*
$(CF_3SO_2)_2O$	Trifluoromethanesulfonic anhydride	80.5, 84							*29, 36, 116*	ir *116*
$CF_3SO_3CH_3$	Methyl trifluoromethanesulfonate	99					1.3238	25	*29, 114*	ir *114, 116*
$CF_3SO_2SCF_3$	Trifluoromethyl trifluoromethanethiolsulfonate	70					1.3480	17	*140*	ir *140*
CF_3SO_2F	Trifluoromethanesulfonyl fluoride	−21.7 −23	22.2						*29, 114*	ir *114*
CF_3SO_2Cl	Trifluoromethanesulfonyl chloride	31.6 33							*29, 140*	ir *140*

Trifluoromethyl sulfones, etc.

$CF_3SO_2CH_3$	Methyl trifluoromethyl sulfone	130		14.0	1.5141	20	1.3486	20	*29, 116, 308*	ir *114*
$CF_3SO_2CH_2Cl$	Chloromethyl trifluoromethyl sulfone	140		−90	1.6533	20	1.3859	20	*308*	
$CF_2ClSO_2CH_3$	Methyl chlorodifluoromethyl sulfone	165		21	1.5685	20	1.4050	20	*308*	
$(CF_3SO_2)_2CH_2$	Bis(trifluoromethanesulfonyl)methane	191							*29*	ir *116*

The hydrocarbonsulfonyl fluorides are poisonous (*224*) but not extremely toxic (*236*). In some dyes the presence of an —SO_2F group causes a lightening and brightening of the shade (*235*).

Further information regarding the many sulfonyl fluorides not mentioned above may be found in the literature (*62*, *63*, *64*, *114*, *120*, *202*, *261*, *262*, *246*, *287*, *309*).

3. Perfluoroalkanesulfonyl Chlorides, R_fSO_2Cl

Trifluoromethanesulfonyl chloride is produced by: (a) the reaction of trifluoromethanesulfonic acid with phosphorus pentachloride at 100°, (b) the reaction of trifluoromethanesulfenyl chloride, CF_3SCl, with an excess of chlorine in the presence of water (Haszeldine and Kidd, 1955, *140;* see also *29* and *116*).

CF_3SO_2Cl is hydrolyzed only slowly at room temperature. With hot water it is converted to CF_3SO_3H within a few hours. The reaction with NaOH solution is fast at room temperature. It reacts slowly with zinc dust and water to give trifluoromethanesulfinyl ion, $CF_3SO_2^-$. From the solution the salts $CF_3SO_2Na \cdot H_2O$ and $(CF_3SO_2)_2Zn \cdot 3H_2O$ have been prepared (*140*). Trifluoromethanesulfonyl chloride reacts with liquid ammonia to form the amide, $CF_3SO_2NH_2$, and with aniline to give the analide (*29*).

4. *Sulfones*

Methyl trifluoromethyl sulfone, $CH_3SO_2CF_3$, was prepared by Truce *et al.* (1952, *308*) by oxidizing CH_3SCF_3 with CrO_3 in glacial acetic acid at 95°. The compounds $CH_2ClSO_2CF_3$ and $CH_3SO_2CClF_2$ were prepared similarly (*308*). Another method for preparing $CH_3SO_2CF_3$ uses the reaction of CF_3SO_2F with CH_3MgI in ether (*116*). This reaction also produces bis(trifluoromethanesulfonyl)methane, $CF_3SO_2CH_2SO_2CF_3$.

$CH_3SO_2CF_3$ is a colorless odorless liquid which resists hydrolysis (*308*). Infrared spectra are known for $CH_3SO_2CF_3$ and $CF_3SO_2CH_2SO_2CF_3$ (*116*).

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