Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINE COMPOUNDS, INORGANIC, SULFUR

The known binary compounds of sulfur and fluorine range in character from ephemeral to rock-like and provide excellent examples of the influence of electronic and structural factors on chemical reactivity. These marked differences are also reflected in the diversified technological utility.

1. Sulfur Hexafluoride

Sulfur hexafluoride [2551-62-4], SF_6, molecular weight 146.07, is a colorless, odorless, tasteless gas. It is not flammable and not particularly reactive. Its high chemical stability and excellent electrical characteristics have led to widespread use in various kinds of electrical and electronic equipment such as circuit breakers, capacitors, transformers, microwave components, etc (see Electronic materials). Other properties of the gas have led to limited usage in a variety of unique applications ranging from medical applications to space research.

Sulfur hexafluoride was first prepared in 1902 (1). The discovery in 1937 that its dielectric strength is much higher than that of air (2) led to its use as an insulating material for cables, capacitors (3), and transformers (4) (see Insulation, electric). Sulfur hexafluoride has been commercially available as AccuDri, SF_6 (AlliedSignal Inc.) since 1948. It is also produced by Air Products and Chemicals in the United States and by others in Germany, Italy, Japan, and Russia.

1.1. Properties

Sulfur hexafluoride is a good dielectric because a high gas density can be maintained at low temperatures. Properties are given in Table 1.

The vapor pressure of the liquid for the range -50 to 45.6°C and a standard % deviation of ± 0.18 is calculated as (10):

$$\log P_{\mathrm{kPa}} = 0.87652594 - 816.48995/T + 0.029287342T - 0.40107549 \times 10^{-4}\ T^2 + 0.7142667\,\frac{(319.802 - T)}{T}\log(319.802 - T)$$

where T is in Kelvin. Equations for the calculation of sublimation pressure are available (5, 24). Heats of vaporization, calculated from the Clausius-Clapeyron equation (15), are /

Temperature, °C	ΔH_{vap}, kJ/mol (kcal/mol)
45.6	0
40	5.608 (1.340)
20	9.80w (2.344)
0	12.23 (2.923)
−20	13.58 (3.246)
−40	14.94 (3.571)

1.1.1. Chemical Properties

With few exceptions, SF_6 is chemically inert at ambient temperature and atmospheric pressure. Thermodynamically SF_6 is unstable and should react with many materials, including water, but these reactions are kinetically impeded by the fluorine shielding the sulfur. Sulfur hexafluoride does not react with alkali hydroxides, ammonia, or strong acids.

At elevated temperatures SF_6 forms the respective fluorides and sulfides with many metals (25). In quartz, it starts to decompose at 500°C (1); in copper or stainless steel, it is less stable (26). The stability of SF_6 at 200 and 250°C in the presence of aluminum, copper, silicon steel, and mild steel is shown in Table 2 (14). Careful exclusion of moisture from the system improves the stability of sulfur hexafluoride in the presence of most materials.

Sulfur hexafluoride is more stable in arcs (27) than fluorocarbons such as C_2F_6, or refrigerants such as CCl_2F_2, but less stable than CF_4, BCl_3, or SiF_4. Exposed to 1000°C temperatures, SF_6 decomposes to SOF_2 and SF_4 to the extent of 10 mol %. In spite of its decomposition, the dielectric strength of SF_6 remains the same.

The main products of SF_6 arc decomposition in the presence of air are SOF_2, SF_4, and SOF_4 plus metal fluorides and sulfides (28).

1.1.2. Electrical Properties

The electrical properties of SF_6 stem primarily from its effectiveness as an electron scavenger. To accomplish electrical breakdown in a dielectric gas, primary electrons must gain sufficient energy to generate appreciable numbers of secondary electrons on molecular impact. Sulfur hexafluoride interferes with this process by capturing the primary electrons, resulting in the formation of $SF^-{}_6$ or $SF^-{}_5$ ions and F atoms (29):

$$SF_6 \longrightarrow (SF_6^-)^* \longrightarrow SF_6^-$$

$$(SF_6^-)^* \longrightarrow SF_5^- + F$$

where $(SF^-{}_6)^*$ represents an activated complex. This complex is stable against autodissociation during tens of microseconds and thus can be stabilized by collisions.

Although production of $SF^-{}_6$ is the primary process, formation of $SF^-{}_5$ ions increases with temperature, and at 200°C the $SF^-{}_5$:$SF^-{}_6$ ratio is 1:25 (30). In addition to high dielectric strength, SF_6 can rapidly interrupt heavy currents at high voltages. At 550 or 756 kV, circuit breaker ratings can be 38,000 and 5,000 MVA, respectively (31). Both SF_6 and C_2F_6 have a more rapid arc recovery than nitrogen (32); six S—F bonds, mean energy 3.4–3.8 eV, are available for fast energy absorption. Both SF_6 and SF_4 have high stability in arcs (27).

Table 1. Physical Properties[a] of Sulfur Hexafluoride

Property	Value	References
sublimation point, °C	−63.9	5
heat of sublimation, kJ/mol[b]	23.59	6
triple point, °C	−50.52	7
pressure at triple point, kPa[c]	225.31	7
critical temperature, °C	45.55	8, 9
critical pressure, MPa[d]	3.759	9, 10
critical density, g/cm^3	0.737	(10–12)
density, g/cm^3		
solid at −195.2°C	2.863	13
liquid	1.336	10, 14
gas	6.0886×10^{-3}	15
vapor pressure of saturated liquid, MPa[d]	2.3676	15
heat of formation, kJ/mol[b]	−1221.66	
free energy of formation, kJ/mol[b]	−1117.73	16
heat of vaporization, kJ/mol[b]	9.6419	15
entropy, kJ/(mol·K)[b]	291.874	16
heat capacity, J/(mol·K)[b]		
liquid at −43°C	119.5	17
gas	97.234	15
surface tension at −20°C, mN/m(=dyn/cm)	8.02	18
viscosity, mPa·s(= cP)		
liquid	0.277	14
gas	0.01576	17
thermal conductivity, W/(m·K)		
liquid	0.0583	19
gas	0.01415	20
sound velocity, gas, m/s	136	14
refractive index, n_D	1.000783	21
dielectric constant		
liquid	1.81	22
gas	1.00204	23
loss tangent (liquid)	0.001	22

[a] All data refer to 25°C and 101.3 kPa (1 atm), unless otherwise stated.

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

[c] To convert kPa to mm Hg, multiply by 7.5.

[d] To convert MPa to atm, divide by 0.101.

1.2. Paschen's Rule and Breakdown Voltage

As pressure decreases to vacuum conditions, the breakdown voltage (BDV) first decreases, then increases, resulting in a minimum as shown in Figure 1. Table 3 gives BDV data for SF_6 and other dielectrics. For optimum utility of a dielectric, a compromise is needed between low boiling point and high BDV. At 300–400 kPa (3–4 atm), the BDV of SF_6 gas has been shown to be equivalent to that of transformer oil under uniform field conditions (35). The BDV of SF_6 deviates from Paschen's rule as pressure increases. This rule is obeyed well only in the case of uniform fields at pressures up to ca 400 kPa (4 atm).

The description of SF_6 electrical properties needed for practical applications is more complex than knowledge of BDV. Corona-onset voltages (COV) must be considered, particularly for the more usual nonuniform fields. Figure 2 illustrates this for a point-to-plane electrode configuration, where extensive prebreakdown corona occurs before sparkover (36).

Table 2. Stability of Sulfur Hexafluoride in Various Materials of Construction[a]

	Decomposition, %/yr	
Material	200°C	250°C
aluminum		0.006
copper	0.18	1.4
silicon steel	0.005	0.01[b]
mild steel	0.2	ca 2

[a] Ref. 14.

[b] Estimated value.

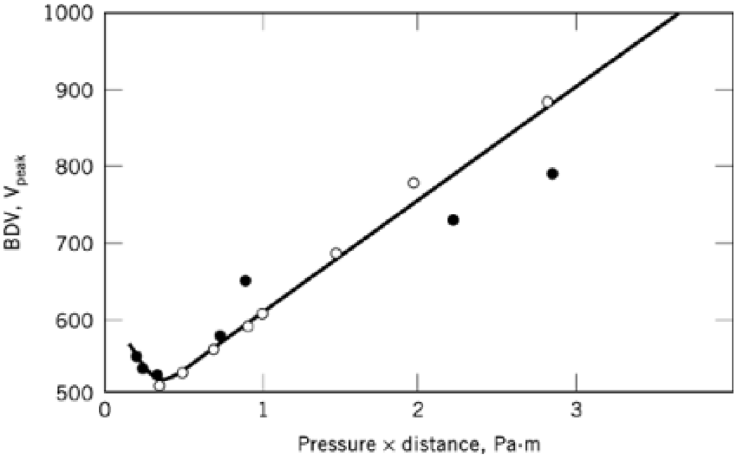


Fig. 1. Paschen's rule plot for SF_6 in uniform electric fields, 60 Hz or dc at 25°C, pressures ≤200 kPa, and a gap ≤0.3 mm. BDV=breakdown voltage. Compiled from References 33 (○) and 34 (●). To convert Pa to μm Hg, multiply by 7.50.

Table 3. Sulfur Hexafluoride Compared with other Dielectrics[a, b]

Compound	Molecular weight	Bp, °C	Relative BDV[c]
SF_6	146.05	−64 (sub)	2.7
CF_2Cl_2	120.9	−29	2.8
CF_3Cl	104.5	−81	1.44
CF_4	88.0	−128	1.14
N_2	28	−194	1.0

[a] Ref. 35.

[b] Conditions: 60 Hz, 0.5 cm gap, 5 cm spheres, at 101.3 kPa (1 atm) and ca 25°C.

[c] BDV = breakdown voltage.

The theory and application of SF_6 BDV and COV have been studied in both uniform and nonuniform electric fields (37). The ionization potentials of SF_6 and electron attachment coefficients are the basis for one set of correlation equations. A critical field exists at 89 kV/(cm·kPa) above which coronas can appear. Relative field uniformity is characterized in terms of electrode radii of curvature. Peak voltages up to 100 kV can be sustained. A second BDV analysis (38) also uses electrode radii of curvature in rod-plane data at 60 Hz, and can be used to correlate results up to 150 kV. With d-c voltages (39), a similarity rule can be used to treat BDV in fields up to 500 kV/cm at pressures of 101–709 kPa (1–7 atm). It relates field strength, SF_6 pressure,

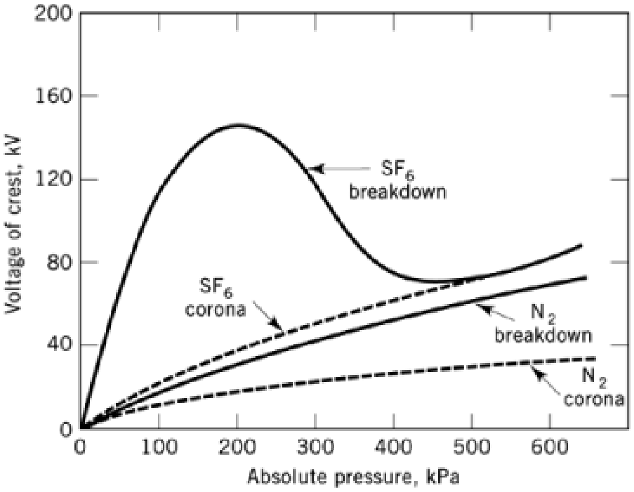


Fig. 2. (—) Sparkover and (— — —) corona onset voltages for SF_6 and N_2 (36). To convert kPa to atm, divide by 101.

and electrode radii to coaxial electrodes having 2.5-cm gaps. At elevated pressures and large electrode areas, a fall-off from this rule appears. The BDV properties of liquid SF_6 are described in the literature (40, 41).

1.2.1. High Frequency Dielectric Strength

Dielectric strength at high frequency is important in microwave power uses such as radar (see Microwave technology). Because SF_6 has zero dipole moment, its dielectric strength is substantially constant as frequency increases. At 1.2 MHz, SF_6 has been shown to have a dielectric strength of 2.3–2.5 relative to N_2 (42). At 3 GHz, SF_6 has about 10 times the power-carrying capacity of air (43), whereas at 9.375 GHz in a waveguide assembly the power-carrying capacity was 7.5 times that of air (42).

1.2.2. Particle Contamination

In assembling large, high voltage equipment such as coaxial lines, contamination by metal particles may occur which may decrease the dielectric strength under various conditions by 5 to 10-fold (44, 45). Metal needles are the worst contaminants and electrostatic traps or adhesive areas have been designed to cope with them (46).

In some cases particles have been added to electrical systems to improve heat removal, for example with an SF_6-fluidized particulate bed to be used in transformers (47). This process appears feasible, using polytetrafluoroethylene (PTFE) particles of low dielectric constant. For a successful application, practical problems such as fluidizing narrow gaps must be solved.

1.3. Manufacture and Quality Control

Sulfur hexafluoride is manufactured by combining sulfur vapor and pure elemental fluorine (48, 49). It is then given a preliminary scrubbing with caustic. Any disulfur decafluoride, S_2F_{10}, formed is decomposed by heating the product to 400°C, to give SF_4 and SF_6. The SF_4 and any remaining lower fluorides of sulfur are removed by a second caustic scrubber. The gas is then dried in a sulfuric acid tower, distilled, and packaged. A routine manufacturing quality-control test establishes the absence of toxic impurities. In this test, mice are exposed to an atmosphere of 80% sulfur hexafluoride and 20% oxygen for 16–20 h and must show no visible effects from the gas.

1.4. Economic Aspects and Shipping

Consumption of SF_6 has increased gradually as dielectric uses have broadened. The estimated worldwide annual consumption for 1992 was about 6000 metric tons. The 1992 U.S. price was ca \$8–15/kg.

Sulfur hexafluoride is packaged as a liquefied gas in DOT 3AA 2015 steel cylinders containing 52 kg. Larger quantities are available in tube trailers containing ca 11,000 kg.

1.5. Specifications and Analytical Methods

Sulfur hexafluoride is made to rigid specifications. Per ASTM D2472-81 (reapproved 1985) (50), the only permissible impurities are traces of air, carbon tetrafluoride (0.05 wt % max), and water (9 ppm by wt max; dew point -45°Cmax).

Sulfur hexafluoride may be analyzed chromatographically using a molecular sieve or a Porapak QS column. Using an electron-capture detector, a sensitivity of 10^{-3} to 10^{-4} ppb is possible (51–53).

1.6. Health and Safety Factors

Sulfur hexafluoride is a nonflammable, relatively unreactive gas that has been described as physiologically inert (54). The current OSHA standard maximum allowable concentration for human exposure in air is 6000 mg/m^3 (1000 ppm) TWA (55). The Underwriters Laboratories classification is Toxicity Group VI. It should be noted, however, that breakdown products of SF_6, produced by electrical decomposition of the gas, are toxic. If SF_6 is exposed to electrical arcing, provision should be made to absorb the toxic components by passing the gas over activated alumina, soda-lime, or molecular sieves (qv) (56).

Because of concerns about the production of the highly toxic S_2F_{10} in arced SF_6 gas, an electrical industry-supported research program was begun in 1992. An interim report indicated that S_2F_{10} may be present in SF_6 gas exposed to electrical discharge, but as of this writing, this could not be precisely quantified (57). The effects of SF_6 on the environment and the Greenhouse effect have been discussed (58).

1.7. Applications

For use as a gaseous dielectric, other specific properties are needed in addition to high breakdown strength, and a compromise must be made between electrical and mechanical requirements. Desirable properties include low toxicity, thermal stability toward materials of construction, good heat transfer, and absence of electrically conducting carbon. Sulfur hexafluoride has a good balance of properties (see Table 1), good dew points, and chemical attributes.

Reviews of gas-phase kinetics (59) and ionization energies (60) have also listed some of the advantages SF_6 enjoys in service as a gaseous dielectric.

1.7.1. Circuit Breakers

Current interruption is essential in high voltage equipment when overloads or other emergencies occur. Circuit breakers consist of relays having contacts equipped with SF_6 jets and high voltage transformers holding fault-sensing coils that can activate a relay contact for each phase of current (61). At 60 Hz, a 765 kV root-mean-square (rms) breaker can have a rating of 50,000 MVA (31). High (1.7 MPa (17 atm)) pressure SF_6 jets extinguish the arcs generated on opening the contacts. Designs of circuit breakers called puffer breakers have encouraged the design of smaller devices, which has extended the use of these types of units (62, 63). Sulfur hexafluoride can also act as the insulation for the sensing transformer and supply pressure to activate the relay contacts. At higher pressures and winter temperatures, heaters serve to prevent SF_6 condensation.

1.7.2. High Voltage Coaxial Lines

Sulfur hexafluoride is the main insulation for power transmission in high voltage coaxial lines which can move power above ground, underground, or underwater (64–66). Voltage ratings range between 65 and 500 kV and higher. Above ground, powers of 300 MVA have been transported. Generally each phase needs one coaxial line, but three-phase lines in one envelope have been developed (64). Lines now handle a-c power, and d-c lines have been tested. To reduce costs, SF_6–N_2 mixtures can be used (67). A long coaxial line having a dielectric constant very near unity is possible before reactive compensation is needed. Usually lines of only a few hundred meters are used, especially where land values are high or where passage under multilane highways or other power lines is necessary.

1.7.3. Mini-Substations

Development of SF_6-insulated lines and circuit breakers made possible development of a compact electric substation that requires one-tenth the land area of conventional designs (64, 68). Other advantages of the ministation are freedom from effects of weather and pollution, and reduced risk of vandalism (69). Substation units in which SF_6 insulates 400 and 500 kV d-c equipment have been developed (70).

1.7.4. Transformers

Units insulated with SF_6 are used mainly in circuit breakers. Some SF_6 power transformers have been designed, but the temperature limitation of ca 200°C restricts this use. The problem in high power units is heat transfer through the gas; this can be alleviated with a fluidized particulate bed (47). Although this approach appears feasible, it has yet to be commercialized.

1.7.5. Other Electrical Uses

Using SF_6 insulation, waveguides can transport 7 to 10-fold more microwave power, which results in doubling radar ranges (21, 42, 43). Voltage ratings in Van de Graaf generators and linear accelerators are also increased by replacing N_2 or air with SF_6 (21). Incorporation of SF_6 in polyethylene-insulated cables increases the starting voltage for tree-formation breakdown processes in the polymer (71, 72).

1.7.6. Nonelectrical Uses

Because of its inertness under normal conditions, SF_6 has been used as a tracer for a variety of studies such as air flow patterns (73), underground pipe leak detection (74), and dispersion of air pollutants (75). It has also been proposed as a refrigerant, either alone (76) or with $CHClF_2$ (77) or CHF_3 as an azeotrope (78). Owing to its low sound velocity, it can improve the performance of loudspeakers at lower pitch registers (79).

At elevated temperatures or under laser radiation, SF_6 becomes a source of fluorine atoms. In the operation of a chemical laser, it abstracts hydrogen from suitable molecules (80, 81). SF_6 is also being used in etching of semiconductor surfaces (82, 83). Mixed with air or CO_2 in the amount of a few tenths of a percent (0.22 vol %), SF_6 protects molten magnesium during its casting process, resulting in reduced slag and an improved metal surface (84, 85). It has also been found useful in removing hydrogen and other gases from aluminum melts (86).

Additional uses include (*1*) filling the enclosed space in double-pane window units to reduce noise and heat transmission (87, 88); (*2*) acting as a source of power from the reaction with lithium to produce heat (89, 90); and (*3*) pressurizing recreation ball packages such as tennis balls to give improved shelf life (91).

2. Sulfur Tetrafluoride

Sulfur tetrafluoride [7783-60-0], SF_4, molecular weight 108.06, is a highly reactive colorless gas that fumes in moist air and has an irritating odor that resembles sulfur dioxide. Interest in this compound as a fluorinating agent was spurred by its unique ability to replace oxygen in compounds containing carbonyl groups. It was first reported in 1929 (92).

2.1. Physical Properties

Sulfur tetrafluoride has the structure of a distorted trigonal bipyramid, the sulfur having hybrid sp^3d orbitals and an unshared electron pair (93). The FSF bond angles have been found to be 101° and 187°, and the bond distances 0.1646 and 0.1545 nm (94).

Selected physical properties are given in Table 4. The nmr data (97) and ir and Raman spectra (98) have also been determined. Thermodynamic functions have been calculated from spectral data (99).

Table 4. Physical Properties of Sulfur Tetrafluoride

Property	Value	Reference
molecular weight	108.055	
melting point, °C	−121.0	95
boiling point, °C	−38	96
critical temperature, °C	90.9	96
surface tension at −73°C, mN/m(=dyn/cm)	257	95
density, liquid, at −73°C, g/mL	1.9190	95
vapor pressure at 25°C, MPa[a]	2.0219	95
heat of vaporization, kJ/mol[b]	26.4	95
heat of formation at 25°C, kJ/mol[b]	−781.1	16
free energy of formation at 25°C, kJ/mol[b]	−740.4	16
entropy at 25°C, J/(mol·K)[b]	300.7	16
dipole moment, C·m[c]	2.11×10^{-30}	94

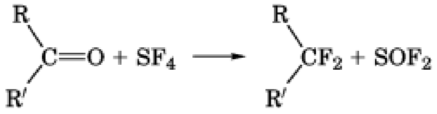
[a] To convert MPa to atm, divide by 0.101.
[b] To convert J to cal, divide by 4.184.
[c] To convert C·m to debye, divide by 3.3366×10^{-30}.

2.2. Chemical Properties

Sulfur tetrafluoride reacts rapidly with water to give hydrofluoric acid and thionyl fluoride [7783-42-8]:

$$SF_4 + H_2O \longrightarrow SOF_2 + 2\ HF$$

With alcohols, mixtures of alkyl fluorides and alkyl ethers are obtained (100). Alcohols bearing electron-withdrawing groups can be converted to the corresponding fluorides in high yield (101). Sulfur tetrafluoride replaces the carbonyl oxygen with fluorine (100, 102).



$$RR'C{=}O + SF_4 \longrightarrow RR'CF_2 + SOF_2$$

Sulfur tetrafluoride reacts with most inorganic oxides and sulfides to give the corresponding fluorides (103):

$$SF_4 + SnS_2 \longrightarrow SnF_4 + 3\ S$$

$$5\ SF_4 + I_2O_5 \longrightarrow 2\ IF_5 + 5\ SOF_2$$

$$3\ SF_4 + UO_3 \longrightarrow UF_6 + 3\ SOF_2$$

Extensive reviews of SF_4 in organic fluorination are available (104, 105).

2.3. Preparation

In the laboratory, sulfur tetrafluoride is made by combining SCl_2 and NaF suspended in acetonitrile at ca 77°C (106). For commercial production, SF_4 is made by direct combination of sulfur with elemental fluorine (107). Commercial applications of SF_4 are limited. It is available from Air Products and Chemicals.

2.4. Toxicity

Sulfur tetrafluoride has an inhalation toxicity comparable to phosgene. The current OSHA standard maximum allowable concentration for human exposure in air is 0.4 mg/m^3 (TWA) (54). On exposure to moisture, eg, on the surface of skin, sulfur tetrafluoride liberates hydrofluoric acid and care must be taken to avoid burns. One case of accidental exposure of electrical workers to decomposed SF_6 gas containing SF_4 has been cited (108).

2.5. Other Sulfur Fluorides

Although eight other binary sulfur fluorides have been synthesized and characterized, proof of the existence of several members of this group was dependent on modern instrumental methods of analysis because of extreme instability. SF_5 and S_2F_{10} are stable, however, the latter is noted for its extreme toxicity. All sulfur fluorides other than SF_6 must be considered extremely toxic.

As a group, these materials have no technological utility because of instability, toxicity, and difficulty of preparation. An excellent review of many of these compounds is available (109).

2.6. Sulfur Pentafluoride

Sulfur pentafluoride [10546-01-7] is thought to be formed during the electrical breakdown of SF_6 and also to be present in plasma reactions involving SF_6. A number of theoretical studies have been reported (110–113).

2.7. Disulfur Decafluoride

Disulfur decafluoride [5714-22-7], S_2F_{10}, is an extremely toxic, colorless, volatile liquid (114). Electron diffraction studies show the molecule to be composed of two octahedral SF_5 groups joined by a sulfur—sulfur bond. The S—F bond distance is 0.156 nm, almost identical to that of SF_6, and the S—S distance is 0.221 nm (115). Table 5 summarizes the known physical properties.

Disulfur decafluoride does not react rapidly with water, mercury, copper, or platinum at ambient temperatures. There is evidence that it slowly decomposes on various surfaces in the presence of water when stored in the vapor state (118). It is decomposed by molten KOH to give a mixture of potassium compounds of sulfur and fluorine. The gas reacts vigorously with many other metals and silica at red heat (114). At ca 156°C it combines with Cl_2 or Br_2 to form SF_5Cl or SF_5Br (119, 120). At ca 200°C, S_2F_{10} is almost completely thermally decomposed into the hexa- and tetrafluoride (121).

Table 5. Physical Properties of S_2F_{10}

Property	Value	Reference
molecular weight	254.13	
melting point, °C	−55	116
boiling point,[a]	28.7	114
critical temperature,[b] °C	165	14
density, liquid, at 25°C, g/cm^3	2.08	114
surface tension at 25°C, mN/m(=dyn/cm)	13.9	114
heat of vaporization, kJ/mol[c]	29.18	114
heat of formation[b,d] at 25°C, kJ/mol[c]	−2.08	117
entropy[b,d] at 25°C, J/(mol·K)[c]	444.93	117
Trouton constant	3.0	114
dielectric constant at 35°C	2.042	114

[a] Vapor pressure calculated. °C
[b] Estimated.
[c] To convert J to cal, divide by 4.184.
[d] Ideal gas.

In the laboratory, S_2F_{10} is prepared by the photochemical reduction of SF_5Cl in the presence of hydrogen (122).

$$2\ SF_5Cl + H_2 \longrightarrow_{h\nu} S_2F_{10} + 2\ HCl$$

The OSHA standard maximum allowable concentration for human exposure in air is 0.10 mg/m^3 (TWA) (55). No commercial uses for this compound have developed.

Because of the extreme toxicity of this material and the possibility it could be present in failed circuit breakers containing decomposed SF_6, several studies have been carried out to develop analytical methods and investigate possible ways to minimize environmental exposure. One method capable of determining S_2F_{10} in the ppb range has been reviewed (123).

Studies on the kinetics of formation of S_2F_{10} and reviews of applicable literature have been reported (124–126). Other work has concentrated on the use of cell culture evaluation methods for assessing cytotoxic activity of SF_6 decomposition products (127, 128). Several laboratories seek to provide methods for accurately determining S_2F_{10} in operating electrical units (57).

2.8. Thiothionyl Fluoride and Difluorodisulfane

Thiothionyl fluoride [1686-09-9], $S{=}SF_2$, and difluorodisulfane [13709-35-8], FSSF, are isomeric compounds which may be prepared as a mixture by the action of various metal fluorides on sulfur vapor or S_2Cl_2 vapor. Chemically, the two isomers are very similar and extremely reactive. However, in the absence of catalytic agents and other reactive species, FSSF is stable for days at ordinary temperatures and $S{=}SF_2$ may be heated to 250°C without significant decomposition (127). Physical properties of the two isomers are given in Table 6. The microwave spectrum of $S{=}SF_2$ has been reported (130).

2.9. Difluoromonosulfane and Difluorodisulfane Difluoride

Difluoromonosulfane [13814-25-0] (sulfur difluoride), SF_2, and its dimer, disulfane tetrafluoride [27245-05-2], SF_3SF, are both extremely unstable compounds which have only a fleeting existence except under rigorously controlled laboratory conditions. These compounds may be prepared by passing SCl_2 vapor over HgF_2 at 150°C (131). Electronic and nmr examinations of SF_2 have been reported (132, 133).

Table 6. Physical Properties of S_2F_2 Isomers[a]

	Value	
Property	FSSF	SSF_2
molecular weight	102.13	102.13
melting point, °C	−133	−164.6
boiling point, °C	15	−10.6
heat of vaporization, kJ/mol[b]	24.80	22.72
entropy of vaporization, J/(mol·K)[b]	86.67	78.08
heat capacity at 25°C, J/(mol·K)[b]	64.0	41.50
entropy[c] at 25°C, J/(mol·K)[b]	299	290.77
heat content at 25°C, kJ/mol[b]	14.017	13.342
free energy, kJ/(mol·K)[b]	72.48	73.26

[a] Ref. 129.

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

[c] Ideal gas.

2.10. Other Fluorosulfanes

Difluorotrisulfane [31517-17-6], FSSSF, and difluorotetrasulfane [31517-18-7], FSSSSF, have been identified as the constituents of the yellow oil obtained when sulfur vapor reacts with AgF. Their existence was demonstrated by nmr and mass spectroscopy (134, 135).

BIBLIOGRAPHY

“Sulfur Compounds” under “Fluorine Compounds, Inorganic” in *ECT* 1st ed., Vol. 6, pp. 732–734, by H. C. Miller, Pennsylvania Salt Manufacturing Co.; “Sulfur Hexafluoride” in *ECT* 1st ed., Suppl. 2, pp. 793–802, by W. Mears, Allied Chemical & Dye Corp.; “Sulfur” under “Fluorine Compounds, Inorganic” in *ECT* 2nd ed., Vol. 9, pp. 664–676, by J. A. Brown, Allied Chemical Corp.; “Sulfur Fluorides” under “Fluorine Compounds, Inorganic–Sulfur” in *ECT* 3rd ed., Vol. 10, pp. 799–811, by R. E. Eibeck and W. Mears, Allied Chemical Corp.

Cited Publications

1. H. Moissan and P. Lebeau, *Ann. Chim. Phys.* **26**, 145 (1902).
2. E. E. Charlton and F. S. Cooper, *Gen. Electr. Rev.* **40**, 438 (1937).
3. B. M. Hokhberg and co-workers, *J. Tech. Phys. (USSR)* **12**, 3 (1942).
4. Brit. Pat. 532,670 (Jan. 29, 1941), (to The British Thompson-Houston Co., Ltd.).
5. W. E. Schumb and E. L. Gamble, *J. Am. Chem. Soc.* **52**, 4302 (1930).
6. D. M. Yost and H. Russell, Jr., *Systematic Organic Chemistry*, Prentice-Hall, Inc., Englewood Cliffs, N.J., 1944, 297–309.
7. V. P. Borisoylekskii, L. I. Strokovskii, and I. S. Zhizuleva *Zh. Fiz. Khim.* **48**, 119 (1974).
8. L. A. Makarevich, E. S. Sokolova, and G. A. Sorena, *Zh. Fiz. Khim.* **42**, 22 (1968).
9. K. E. MacCormack and W. G. Schneider, *Can. J. Chem.* **29**, 699 (1951).
10. W. H. Mears, E. Rosenthal, and J. V. Sinka, *J. Phys. Chem.* **73**, 2254 (1969).
11. L. A. Makarevich and O. N. Sokolova, *Zh. Fiz. Khim.* **47**, 763 (1973).
12. D. Balzarini and P. Palffy, *Can. J. Phys.* **52**, 2007 (1974).
13. T. G. Pearson and R. L. Robinson, *J. Chem. Soc.*, 1427 (1933).
14. Unpublished data, Allied Chemical Corp., Morristown, N.J., 1993.
15. E. Rosenthal, *Sulfur Hexafluoride–Thermodynamic Properties*, unpublished study, Specialty Chemicals Div., Allied Chemical Corp., Morristown, N.J., 1969.

16. *JANAF Thermochemical Tables, NSRDS-NBS-37*, 2nd ed., National Bureau of Standards, Washington, D.C., June 1971.
17. A. Eucken and E. Schroder, *Z. Phys. Chem.* **B41**, 307 (1938).
18. J. Neudorffer, *Ann. Chim. (Paris)* **8**, 501 (1953).
19. P. Grassman and W. Tauscher, *Allied Chemical Research Contract*, Institute of Heat and Engineering, EIDG Technical University, Zurich, Switzerland, 1967.
20. W. A. Tauscher, *Kaltetech.-Klimatisierin* **24**, 67 (1972).
21. *Technical Bulletin SFBR-1 (Sulfur Hexafluoride)*, Specialty Chemicals Division, Allied Chemical Corp., Morristown, N.J., 1973.
22. D. Berg, *J. Chem. Phys.* **31**, 572 (1959).
23. H. E. Watson, G. C. Rao, and K. L. Ramaswamy, *Proc. R. Soc. Ser. A* **132**, 569 (1931).
24. B. Genot, *J. Chim. Phys. Physiochem. Biol.* **68**, 111 (1971).
25. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd ed., Wiley-Interscience, New York, 1962, p. 419.
26. D. K. Padma and A. R. Vasuderamurthy, *J. Fluor. Chem.* **5**, 181 (1975).
27. J. P. Manion, J. A. Philosophos, and M. B. Robinson, *IEEE Trans., Trans. Electr. Insul.* **E1-2**(1), 1 (Apr. 1967).
28. C. Boudene and co-workers, *Rev. Gen. Electr.* (Special No.), 45 (June 1974).
29. R. L. Champion, *Gaseous Dielectric 6,* Proceedings of the 6th International Symposium, 1990, (Pub. 1991), 1–8.
30. F. C. Fehsenfeld, *J. Chem. Phys.* **53**, 2000 (1970).
31. R. N. Yerkley and C. F. Cromer, *IEEE Trans., Power Appar. Syst.* **89**(8), 2065 (1970).
32. M. Hudis, *CP74-090-7, IEEE Power Engineering Society, Winter Meeting, New York,* Jan. 27–Feb. 1, 1974.
33. G. Luxa and co-workers, *Item D. Paschen Curve for* SF_6*, 1975 CIGRE International Conference on Large High Tension Electrical Systems.*
34. S. Schreier, *IEEE Trans., Power Appar. Syst.* **83**, 468 (1964).
35. P. R. Howard, *Proc. Inst. Elect. Eng.* **104**(A), 123 (1957).
36. C. N. Works and T. W. Dakin, *Trans. AIEE* **72**(1), 682 (1953).
37. T. Nitta and Y. Shibuya, *IEEE Trans., Power Appar. Syst.* **90**, 1965 (1971).
38. A. A. Azer and P. P. Comsa, *IEEE Trans. Electr. Insul.* **8**(4), 136 (1973).
39. I. M. Bortnik and C. M. Cooke, *IEEE Trans., Power Appar. Syst.* **91**, 2196 (1972).
40. C. N. Works, T. W. Dakin, and R. W. Rogers, *N.A.S.N.R.C. Publ.* (1080), 69 (1963).
41. Y. V. Torshin, Conference Paper 118, *Third International Conference on Gas Discharges,* IEE, London, Sept. 9–12, 1974.
42. T. Anderson and co-workers, *AIEE Conf. Paper 52–82,* 1957.
43. J. W. Sutherland, *Electron. Eng.*, 538 (1955).
44. C. M. Cook, R. E. Wootton, and A. H. Cookson, *IEEE Trans., Power Appar. Syst.* **96**(3), 768 (1977).
45. A. H. Cookson, O. Farish, and G. M. Sommerman, *IEEE Trans., Power Appar. Syst.* **9**(4), 1329 (1972).
46. J. G. Trump, *IEEE Trans. Nucl. Sci.* **14**, 113 (1962).
47. *Gas Insulated Fluidized Bed Transformer, Final Report EL-302*, Project 479-1, Electric Power Research Inst. (EPRI), Buffalo, N.Y., May 1977.
48. U.S. Pat. 3,336,111 (Aug. 15, 1967), W. E. Watson, H. G. Tepp, and M. H. Cohen (to Allied Chemical Corp.)
49. E. P. 87338 (Aug. 31, 1983) M. Jaccaud and A. J. F. Ducouret (to PCUK-Ugine Kuhlmann-Atochem).
50. *ASTM D2472-81* (reapproved 1985), American Society of Testing and Materials, Philadelphia, Pa., 1981.
51. J. E. Lovelock and S. B. Lipsky, *J. Am. Chem. Soc.* **82**, 860 (1960).
52. *Ibid.*, 431 (1960).
53. P. G. Simonds and co-workers, *Anal. Chem.* **44**, 860 (1972).
54. D. Lester and L. A. Greenberg, *Arch. Ind. Hyg. Occup. Med.* **2**, 348 (1950).
55. *Threshold Limit Values for Chemical Substances and Physical Agents*, American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1990–1991.
56. W. C. Schumb, J. G. Trump, and G. L. Priest, *Ind. Eng. Chem.* **41**, 1348 (1949).
57. D. R. James, Technical Note No. 1, *Cooperative Research and Development Agreement (CRADA), Investigation of* S_2F_{10} *Production and Mitigation in Compressed* SF_6*-Insulated Power System,* Oak Ridge National Laboratory, Oak Ridge, Tenn., Dec. 28, 1992.
58. L. Niemayer, F. Y. Chu, *IEEE Trans. Elec. Insul.* **27**(1), 184–187 (Feb. 1992).

59. J. T. Herron, *Int. J. Chem. Kinet.* **19**(2) 129–42 (1987).
60. M. L. Lanferd and co-workers, *Int. J. Mass. Spectrum Ion Processes*, **98**(2) 147–53 (1990).
61. T. Ushio, I. Shimura, and G. Tominago, *IEEE Trans., Power Appar. Syst.* **89**, 2615 (1970).
62. U.S. Pat. 5,059,753 (Oct. 22, 1991), S. R. Hamm (to Cooper Industries).
63. U.S. Pat. 4,752,860 (June 21, 1988), A. Giboulet and P. Romanet (to Merlin-Gerin SA).
64. S. D. Barrett, *The A to Z of* SF_6*, Special Report Electric Light and Power,* TID ed., Dec. 1972.
65. *Electr. World Trans. Dist.* **54**, (Feb. 15, 1972).
66. B. O. Pedersen, H. C. Doepken, and D. C. Bolin, *IEEE Trans., Power Appar. Syst.* **90**, 2631 (1971).
67. R. Nakata and co-workers, *An Underground High Voltage Direct Current Transmission Line, IEEE Underground Distribution and Transmission Conference, Dallas, Tex., Apr. 1–5, 1974.*
68. *Electr. World* **61**, (Feb. 23, 1976).
69. *IEEE Trans. Power Appar. Syst.* **94**, (1975).
70. E. E. Fischer, A. Glassanos, and N. G. Hingorani, *Electr. World Trans. Dist.* **40**, (Feb. 1, 1977).
71. T. Kojima and co-workers, *Showa Wire Cable Rev.* **221**, 11 (1972).
72. U.S. Pat. 4,783,576 (Nov. 8, 1988), W. G. Lawson and D. A. Silver (to Pirelli Cable Co.)
73. P. J. Drivas and F. H. Shair, *Atmos. Environ.* **8**, 1155 (1974).
74. U.S. Pat. 5,046,353 (Sept. 10, 1991), G. M. Thompson (to Tracer Research Corp.)
75. B. K. Lamb, D. E. Stock, HTD *(Am. Soc. Mech. Eng.)* **152** *(Mixed Convert Enveron Flows)* 55–59, (1990).
76. R. Plank, *Kaltetechnik* **8**, 302 (1956).
77. U.S. Pat. 3,642,639 (Feb. 15, 1972), K. P. Murphy and R. F. Stahl (to Allied Chemical Corp.).
78. U.S. Pat. 3,719,603 (Mar. 6, 1973), R. F. Stahl (to Allied Chemical Corp.).
79. U.S. Pat. 2,797,766 (July 2, 1957), H. W. Sullivan (to D. Bogen and Co.).
80. D. N. Kaye, *New Sci.* **14**, 65 (1971).
81. D. J. Spenser and co-workers, *Int. J. Chem. Kinet.* **1**, 493 (1969).
82. U.S. Pat. 4,680,087 (July 14, 1987), S. M. Bobbio (to AlliedSignal).
83. U.S. Pat. 4,980,018 (Dec. 25, 1990), Mu Xiao-Chun and Multani Jagin (to Intel Corp.).
84. J. W. Fruehling and J. D. Hanawalt, *Am. Foundry Soc. Trans.* **16**, 159 (1969).
85. O. Schlem, *Giesserei* **19**, 558 (1971).
86. U.S. Pat. 4,959,010 (Sept. 25, 1990), R. R. Corns and co-workers (to AGA AB).
87. U.S. Pat. 4,800,693 (Jan. 31, 1989), I. Fasth and J. Karlsen (to Barrier HB).
88. Fr. Pat. 2,529,609 (Jan. 6, 1984), M. Rehfeld (to Saint-Gobain Vitrage).
89. U.S. Pat. 4,959,566 (Sept. 25, 1990) Dobran Flavio
90. S. H. Chan and co-workers, *23rd Symposium on Internal Combustion. Proceedings, 1990* (Pub. 1991), 1139–1146.
91. U.S. Pat. 4,358,111 (Nov. 11, 1982), J. J. Oransky and co-workers (to Air Products and Chemicals).
92. J. Fischer and W. Jaenckner, *Z. Angew. Chem.* **42**, 810 (1929).
93. F. H. Cotton, J. W. George, and J. S. Waugh, *J. Chem. Phys.* **28**, 994 (1958).
94. W. M. Tolles and W. D. Gwinn, *J. Chem. Phys.* **36**, 1119 (1962).
95. E. Brown and P. L. Robinson, *J. Chem. Soc.*, 3147 (1955).
96. *Sulfur Tetrafluoride, Tech. Bulletin, 2B*, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1946.
97. J. Bacon and R. J. Gillespie, *Can. J. Chem.* **41**, 1016 (1963).
98. K. O. Christe and co-workers, *Spectrochim. Acta* **32A**, 1141 (1976).
99. M. Radharkrishnan, *Z. Naturforsch.* **18a**, 103 (1963).
100. W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.* **82**, 543 (1960).
101. U.S. Pat. 2,980,740 (Apr. 18, 1961), (to E. I. du Pont de Nemours & Co., Inc.).
102. U.S. Pat. 2,859,245 (Nov. 4, 1958), W. C. Smith (to E. I. du Pont de Nemours & Co., Inc.).
103. A. L. Oppegard and co-workers, *J. Am. Chem. Soc.* **82**, 3835 (1960).
104. C. L. J. Wang, *Org. React. (N.Y.)* **34**, 319–400 (1985).
105. W. Dmowski, *J. Fluorine Chem.* **32**(3) 255–282 (1986).
106. F. S. Fawcett and C. W. Tullock in J. Kleinberg, ed., *Inorganic Syntheses*, Vol. **7**, McGraw-Hill Book Co., Inc., New York, 1963, 119–124.
107. U.S. Pat. 3,399,036 (Aug. 27, 1968), (to Air Products and Chemicals, Inc.).
108. A. Kraut, R. Lilis, *Br. J. Ind. Med.* **47**(12) 829–832 (1990).

109. F. Seel in H. J. Emeleus and G. G. Sharpe, eds., *Advances in Inorganic and Radio Chemistry*, Vol. **16**, Academic Press, Inc., New York, 1974, 297–333.
110. J. T. Herron, *Proceedings of the 5th International Symposium on Gaseous Dielectricics,* 1987, 199–204.
111. M. Ticky and co-workers, *Int. J. Mass. Spectrum Ion Processes*, **76**(3) 231–235 (1987).
112. W. L. Sieck and P. J. Ausloos, *J. Chem. Phys.* **93**(11) 8374–8 (1990).
113. I. C. Plant and K. R. Ryan, *Plasma Chem. Plasma Process.*, **6**(3) 247–258 (1986).
114. K. B. Denbigh and R. W. Gray, *J. Chem. Soc.*, 1346 (1934).
115. R. B. Harvey and S. H. Bauer, *J. Am. Chem. Soc.* **75**, 2840 (1953).
116. N. R. S. Hollies and R. L. McIntosh, *Can. J. Chem.* **29**, 494 (1951).
117. G. Pass, *J. Appl. Chem.* **19**, 77 (1969).
118. J. K. Olthoff and co-workers, *Conference Record of the IEEE International Symposium on Electrical Insulation,* 1990, 248–252.
119. B. Cohen and A. G. MacDiarmid, *Inorg. Chem.* **4**, 1782 (1965).
120. T. A. Kovacina, A. D. Berry, and W. B. Fox, *J. Fluor. Chem.* **7**, 430 (1976).
121. W. R. Trost and R. L. McIntosh, *Can. J. Chem.* **29**, 508 (1951).
122. H. L. Roberts, *J. Chem. Soc.*, 3183 (1962).
123. J. K. Olthoff and co-workers, *Anal. Chem.* **63**(7) 726 (1991).
124. F. Y. Chu and co-workers, *Conference Record of the IEEE International Symposium on Electrical Insulation,* 1988, 131–134.
125. J. T. Herron, *Int. J. Chem. Kinet.* **19**(2) 129–142 (1987).
126. J. T. Herron, *J. Phys. Chem. Ref. Data* **16**(1) 1–6 (1987).
127. G. D. Griffin and co-workers, *Toxicol. Environ. Chem.* **9**(2) 139–166 (1984).
128. G. D. Griffin, *IEE Proc. Part A*, **137**(4) 221–227 (1990).
129. F. Seel, *Chimia* **22**, 79 (1968).
130. R. W. Davis, *J. Mol. Spectrosc* **116**(2) 371–383 (1986).
131. F. Seel, H. Heinrich, and W. Gombler, *Chimia* **23**, 73 (1969).
132. W. Gombler and co-workers, *Inorg. Chem.* **29**(14) 2697–8 (1990).
133. R. J. Glinski and co-workers, *J. Chem. Phys. Chem.* **94**(16) 6196–6201 (1990).
134. F. Seel and co-workers, *Z. Anorg. Allgem. Chem.* **380**, 262 (1971).
135. F. Seel, R. Budenz, and D. Werner, *Ber.* **97**, 1369 (1964).

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