Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINE COMPOUNDS, INORGANIC, FLUOROSULFURIC ACID

Fluorosulfuric acid [7789-21-1], HSO_3F, is a colorless-to-light yellow liquid that fumes strongly in moist air and has a sharp odor. It may be regarded as a mixed anhydride of sulfuric and hydrofluoric acids. Fluorosulfuric acid was first identified and characterized in 1892 (1). It is a strong acid and is employed as a catalyst and chemical reagent in a number of chemical processes, such as alkylation (qv), acylation, polymerization, sulfonation, isomerization, and production of organic fluorosulfates (see Friedel-crafts reactions).

1. Properties

Selected physical properties of fluorosulfuric acid are shown in Table 1. Fluorosulfuric acid is soluble in acetic acid, ethyl acetate, nitrobenzene, and diethyl ether, and insoluble in carbon disulfide, carbon tetrachloride, chloroform, and tetrachloroethane. Many inorganic and organic materials dissolve in fluorosulfuric acid; the physical and chemical properties of such solutions have been extensively investigated (5–8). The structure of fluorosulfuric acid has been determined (9), and the ir, Raman, and nmr spectra have been reported (10). The solution of antimony pentafluoride [7783-70-2] in fluorosulfuric acid results in a superacid possessing protonating power orders of magnitude greater than 100% sulfuric acid. Extensive studies on the properties of superacid compositions containing fluorosulfuric acid have been published (11, 12).

Fluorosulfuric acid is stable to heat up to decomposition at about 900°C (13), where vapor-phase dissociation into hydrogen fluoride and sulfur trioxide probably occurs. Reviews of the chemistry and properties of fluorosulfuric acid have been published (14–16).

1.1. Reactions

The reaction of fluorosulfuric acid and water is violent and exothermic; it proceeds as follows:

$$\textit{Fasthydrolysis} \qquad HSO_3F + H_2O \rightleftharpoons H_2SO_4 + HF$$

$$\textit{Ionization} \qquad HSO_3F + H_2O \rightleftharpoons H_3O + SO_3F^-$$

$$\textit{Slowhydrolysis} \qquad SO_3F^- + H_2O \rightleftharpoons HSO_4^- + HF$$

The extent of the initial hydrolysis depends on temperature and how the water is added. Hydrolysis is reduced at slower addition rates and lower temperatures. The hydrolysis subsequent to the initial fast reaction is slow,

Table 1. Physical and Chemical Constants of Fluorosulfuric Acid

Property	Value[a]	References
molecular weight	100.07	
boiling point, °C	162.7	(1, 2)
freezing point, °C	−88.98	3
density, g/mL	1.726	2
viscosity, mPa·s(=cP)	1.56	2
dielectric constant	ca 120	2
specific conductance, $(\Omega\cdot m)^{-1}$	1.085×10^{-6}	2
heat of formation,[b] ΔH_f, kJ/mol[c]	792.45	4

[a] All values at 25°C.
[b] From SO_3 and HF.
[c] To convert kJ to kcal, divide by 4.184.

Table 2. Reactions of Fluorosulfuric Acid and Inorganic Compounds

	Product		
Reactant	Name	Formula	References
nitrogen oxides	nitrosyl fluorosulfate, nitryl fluorosulfate	FSO_3NO, FSO_3NO_2	(26, 27)
H_3BO_3	boron trifluoride	BF_3	28
$KClO_4$	perchloryl fluoride	ClO_3F	29
$KMnO_4$	manganese(VII) fluoride trioxide	MnO_3F	30
As_2O_3	arsenic trifluoride	AsF_3	31
As_2O_5	arsenic pentafluoride	AsF_5	31
CrO_3	difluorodioxochromium (VI)	CrO_2F_2	32
P_4O_{10}	phosphoryl fluoride	POF_3	31
H_2S in ethanol	monothiosulfuric acid	$H_2S_2O_3$	33

presumably because part of the acid is converted to fluorosulfate ions which hydrolyze slowly even at elevated temperatures. The hydrolysis in basic solution has also been studied (17). Under controlled conditions, hydrates of HSO_3F containing one, two, and four molecules of water have been observed (18, 19).

The pure acid does not react in the cold with sulfur, selenium, tellurium, carbon, silver, copper, zinc, iron, chromium, or manganese, but slowly dissolves mercury and tin (20). At higher temperatures, lead, mercury, tin, and sulfur react rapidly, eg:

$$S + 2\ HSO_3F \longrightarrow 3\ SO_2 + 2\ HF$$

Precipitated (hydrated) silica reacts vigorously with fluorosulfuric acid to give silicon tetrafluoride [7783-61-1] (21), but glass (qv) is not attacked in the absence of moisture (20). Alkali and alkaline-earth metal chlorides are readily converted to fluorosulfates by treatment with fluorosulfuric acid (7, 13, 22, 23).

Electrolysis of fluorosulfuric acid produces either $S_2O_6F_2$ [13709-32-5] (24) or SO_2F_2 [13036-75-4] plus OF_2 (25), depending on specific conditions. Various reactions of fluorosulfuric acid with inorganic compounds are shown in Table 2, and with organic compounds in Table 3.

Other studies which have been reported describe unusual chemistry such as HSO_3F–$Nb(SO_3F)_5$ systems (42). Also the unique properties of fluorosulfuric acid have been found to provide unusual solvent systems, which can vary properties such as acidity, heats of solution, enthalpy, and heats of neutralization (43).

Fluorosulfuric acid may be used to prepare diazonium fluorosulfates, $ArN^+{}_2SO_3F^-$ (44), which decompose on heating to give aryl (Ar) fluorosulfates (36, 45). Aryl fluorosulfates are also obtained from arylsulfonyl

Table 3. Reactions of Fluorosulfuric Acid and Organic Compounds

	Product		
Reactant	Name	Formula	References
benzene[a]	benzenesulfonic acid	$C_6H_5SO_3H$	(20, 34)
	diphenyl sulfone	$(C_6H_5)_2SO_2$	34
	benzenesulfonyl fluoride	$C_6H_5SO_2F$	35
aliphatic amines	amidosulfuric acids	R_2NSO_3H or $RNHSO_3H$	36
aromatic compound	arylsulfonyl fluorides[b]	$ArSO_2F$	
carboxylic acids	acid fluorides	RCOF	37
alcohol or alkene	alkyl fluorosulfates	$ROSO_2F$	(20, 38, 39)
perhaloolefins or perhaloalkyl iodides	perhaloalkyl fluorosulfates	R_fOSO_2F	(40, 41)

[a] Product is dependent on reaction conditions and proportions of reagents.
[b] Ar represents an aryl group.

chlorides and fluorosulfuric acid (35). Alkyl and other organofluorosulfates form during electrolysis of fluorosulfuric acid in the presence of organic species (46, 47).

1.2. Preparation and Manufacture

Fluorosulfuric acid, first prepared by combining anhydrous HF and cooled, anhydrous SO_3 in a platinum container (1), has also been prepared from ionic fluorides or fluorosulfates and sulfuric acid (20, 48). The reaction of chlorosulfuric acid (qv) with ionic fluorides also gives fluorosulfuric acid (49).

Commercially, fluorosulfuric acid is made by processes utilizing the product as a solvent. Solutions of HF and SO_3 in fluorosulfuric acid are mixed in stoichiometric quantities, or SO_3 and HF are separately introduced into a stream of fluorosulfuric acid to produce essentially pure HSO_3F. Some of the product is then recycled (50, 51).

Fluorosulfuric acid can be very corrosive. A study of the corrosive properties of fluorosulfuric acid during preparation and use showed carbon steel to be acceptable up to 40°C, stainless steel up to 80°C, and aluminum alloys up to 130°C (52).

1.3. Economic Aspects

U.S. manufacturers of fluorosulfuric acid are AlliedSignal and Du Pont. These companies have a combined annual capacity estimated at 20,000 metric tons, most of which is used internally although some merchant sales exist. Fluorosulfuric acid is shipped in tank cars.

1.4. Specifications and Analysis

Commercial fluorosulfuric acid contains approximately 98% HSO_3F and approximately 1% H_2SO_4 and lesser amounts of sulfur trioxide and dioxide. No free HF is present.

The free sulfur trioxide can be titrated with water; the end point is determined conductimetrically. The sulfuric acid content is determined from the specific conductivity of the liquid at the point in the titration where no free SO_3 or excess water is present. If the presence of HF is suspected, a known amount of SO_3 is added to the acid and the excess SO_3 is determined as above. The content of another common impurity, SO_2, may be determined iodometrically in a dilute, aqueous solution.

1.5. Health and Safety Factors

Fluorosulfuric acid is a strong acid capable of causing severe burns similar to those experienced with sulfuric and hydrofluoric acids. In addition, the fumes of fluorosulfuric acid are extremely irritating, and breathing of the fumes is to be avoided. Precautions and first aid measures generally observed in handling strong sulfuric acid and hydrofluoric acid are applicable to fluorosulfuric acid. Small containers of fluorosulfuric acid should be well cooled before opening and precautions taken to relieve any gas pressure that may have developed. In the laboratory, fluorosulfuric acid may be handled in glass if water is not present; otherwise, containers of inert polymers or platinum should be used. For larger-scale equipment, iron or carbon steel (not stainless steel) may be used. Material safety data sheets and other literature from manufacturers describe additional precautions in handling large quantities of fluorosulfuric acid.

1.6. Uses

Fluorosulfuric acid serves as catalyst in the alkylation (qv) of branched-chain paraffins (53–58) and aromatic compounds (59), and in the polymerization of monoolefins (60) and rosin (61). Addition of strong Lewis acids, such as SbF_5, TaF_5, and NbF_5, to fluorosulfuric acid markedly increases the system acidity and catalytic activity (62–69). Other examples which show the marked catalytic effect of fluorosulfuric acid alone or in systems including SbF_5, etc, are the synthesis of methyl *tert*-butyl ether (70), the stereospecific formation of 2-naphthol (71), formation of aromatic aldehydes using CO (72), and polymerization of tetrahydrofuran (73, 74) (see CAtalysis).

As a reagent, fluorosulfuric acid has been employed in the preparation of boron trifluoride (28), silicon tetrafluoride (75, 76), alkyl fluorosulfates (20, 38), arenesulfonyl fluorides (35), acyl fluorides (77), sulfamic acid (78), and diazonium fluorosulfates (44). Among its other uses are the removal of small amounts of organic fluorides from petroleum alkylate made by the hydrogen fluoride process (79), the removal of HF from process exhaust gases (80), the removal of HF from F_2 (81), and as a constituent of baths for electropolishing metals (82, 83) and glass polishing (84).

1.7. Derivatives

The nonmetallic inorganic derivatives of fluorosulfuric acid are generally made indirectly, although complex fluorosulfates of the Group 15 (V) elements and of xenon can be made directly (85, 86), as can the NO^+ and $NO^+{}_2$ salts (26, 27).

Peroxydisulfuryl difluoride [13709-32-5], FSO_2OOSO_2F, prepared from fluorine and SO_3 (87), is a ready source of fluorosulfate radicals, $FSO_2O\cdot$, (88) which react with many substances to form stable fluorosulfates (89, 90). By using the route

$$X_2 + nS_2O_6F_2 \longrightarrow 2\,X(OSO_2F)_n$$

where $n = 1$ or 3, compounds of the type $FOSO_2F$ [13536-85-1] (91), $BrOSO_2F$ [13997-93-8], and $I(OSO_2F)_3$ [13709-37-0] (92) have been prepared. Fluorosulfates of most metallic elements have been prepared but none have any commercial significance. The physical properties of some fluorosulfates are summarized in Table 4.

Ammonium fluorosulfate is produced from ammonium fluoride by reaction with sulfur trioxide, oleum, or potassium pyrosulfate, $K_2S_2O_7$ (48). Solutions of ammonium fluorosulfate show little evidence of hydrolysis and the salt may be recrystallized from hot water. Ammonium fluorosulfate absorbs anhydrous ammonia to form a series of liquid amines that contain 2.5–6 moles of ammonia per mole of salt (77).

Sodium fluorosulfate may be prepared by the action of fluorosulfuric acid on powdered, ignited sodium chloride (13) or of sulfur trioxide on sodium fluoride (48). In general, the alkali metal fluorosulfates may be

Table 4. Physical Properties of Some Fluorosulfates

				Solubility	
Salt	CAS Registry Number	Appearance	Mp, °C	Water[a]	Other solvents[a]
NH_4SO_3F	[13446-08-7]	long colorless needles	245	s	sl s ethanol; v s methanol
$LiSO_3F$	[13453-75-3]	white powder	360	v s	v s ethanol, ether, acetone, amyl alcohol, ethyl acetate; i ligroin
$LiSO_3F{\cdot}3H_2O$		long shiny needles	60–61		
$NaSO_3F$	[14483-63-7]	shiny leaflets, hygroscopic		s	s ethanol, acetone; i ether
KSO_3F	[13455-22-6]	short white prisms	311	6.9[b]	sl s methanol
$RbSO_3F$	[15587-05-0]	colorless needles	304	s	sl s methanol
$CsSO_3F$	[13530-70-6]	colorless rhombic	292	2.23[b]	

[a] i = insoluble; sl s = slightly soluble; v s = very soluble.
[b] In g/100 mL water.

prepared from the ammonium salt by evaporating a solution containing that salt and an alkali metal hydroxide (77). The solubilities of some Group 1 and 2 fluorosulfates in fluorosulfuric acid have been determined (93).

BIBLIOGRAPHY

"Fluosulfonic Acid" under "Fluorine Compounds, Inorganic" in *ECT* 1st ed., Vol. 6, pp. 734–738, by W. S. W. McCarter, Pennsylvania Salt Manufacturing Co.; "Fluorosulfuric Acid" under "Fluorine Compounds, Inorganic" in *ECT* 2nd ed., Vol. 9, pp. 676–681, by R. E. Eibeck, Allied Chemical Corp.; "Fluorosulfuric Acid" under "Fluorine Compounds, Inorganic–Sulfur" in *ECT* 3rd ed., Vol. 10, pp. 812–817, by R. E. Eibeck, Allied Chemical Corp.

Cited Publications

1. T. E. Thorpe and W. Kirman, *J. Chem. Soc.* 921 (1892).
2. J. Barr, R. J. Gillespie, and R. C. Thompson, *Inorg. Chem.* **3**, 1149 (1964).
3. R. J. Gillespie, J. B. Milne, and R. C. Thompson, *Inorg. Chem.* **5**, 468 (1966).
4. G. W. Richards and A. A. Woolf, *J. Chem. Soc. A*, 1118 (1967).
5. A. A. Woolf, *J. Chem. Soc.*, 2840 (1954); A. A. Woolf, *J. Chem. Soc.*, 433 (1955).
6. R. J. Gillespie and co-workers, *Can. J. Chem.* **40**, 675 (1962); R. J. Gillespie and co-workers, *Can. J. Chem.* **41**, 148, 2642 (1963); R. J. Gillespie and co-workers, *Can. J. Chem.* **42**, 502, 1433 (1964).
7. R. J. Gillespie and co-workers, *Inorg. Chem.* **3**, 1149 (1964).
8. R. J. Gillespie and co-workers, *Inorg. Chem.* **4**, 1641 (1965); R. J. Gillespie and co-workers, *Inorg. Chem.* **8**, 63 (1969).
9. K. Bartmann and D. Mootz, *Acta Crystallogr., Sect. C* C46(2), 319–320 (1990).
10. R. J. Gillespie and E. A. Robinson, *Can. J. Chem.* **40**, 644, 675 (1962); R. Savoie and P. A. Giguere, *Can. J. Chem.* **42**, 277 (1964).
11. B. Carre and J. Devynck, *Anal. Chim. Acta* **159**, 149–158 (1984).
12. V. Gold and co-workers, *J. Chem. Soc., Perkin Trans.* **2**(6) 859–864 (1985).
13. O. Ruff, *Chem. Ber.* **47**, 646 (1914).
14. R. J. Gillespie, *Accounts. Chem. Res.* **1**(7), 202 (1968).
15. R. C. Thompson in G. Nickless, ed., *Inorganic Sulphur Chemistry*, Elsevier, Amsterdam, the Netherlands, 1968, 587–606.
16. A. W. Jache in H. J. Emeleus and A. G. Sharpe, eds., *Advances in Organic Chemistry and Radiochemistry*, Vol. **16**, Academic Press, Inc., New York, 1974, 177–200.
17. I. G. Ryss and A. Drabkina, *Kinet. Katal.* **7**, 319 (1966).
18. R. C. Paul, K. K. Paul, and K. C. Malhotra, *Inorg. Nucl. Chem. Lett.* **5**, 689 (1969).
19. D. Mootz, K. Bartmann, *Z. Anorg. Allg. Chem.* **592**, 171–178 (1991).

20. J. Meyer and G. Schramm, *Z. Anorg. Allg. Chem.* **206**, 24 (1932).
21. L. J. Belf, *Chem. Ind. (London)*, 1296 (1955).
22. P. Bernard, Y. Parent, and P. Vast, C. R. *Acad. Sci. Ser. C* **269**, 767 (1969).
23. E. Kemnitz and D. Hass, *Z. Chem.* **30**(7), 264–265 (1990).
24. J. M. Shreeve and G. H. Cady, *J. Am. Chem. Soc.* **83**, 4521 (1961).
25. H. Schmidt and H. D. Schmidt, *Z. Anorg. Allg. Chem.* **279**, 289 (1955).
26. D. R. Goddard, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2559 (1950).
27. W. Lange, *Chem. Ber.* **60B**, 967 (1927).
28. U.S. Pat. 2,416,133 (Feb. 18, 1947), D. Young and J. Pearson (to Allied Chemical Corp.).
29. G. Barth-Wehrenalp, *J. Inorg. Nucl. Chem.* **2**, 266 (1956).
30. A. Engelbrecht and A. V. Grosse, *J. Am. Chem. Soc.* **76**, 2042 (1954).
31. E. Hayek, A. Aignesberger, and A. Engelbrecht, *Monatch. Chem.* **86**, 470735 (1955).
32. A. Engelbrecht, *Angew. Chem. Int. Ed. Engl.* **4**, 641 (1965).
33. M. Schmidt and G. Talsky, *Z. Anorg. Allg. Chem.* **303**, 210 (1960).
34. J. H. Simons, H. J. Passino, and S. Archer, *J. Am. Chem. Soc.* **63**, 608 (1941).
35. W. Steinkopf and co-workers, *J. Prakt. Chem.* **117**, 1 (1927).
36. Ger. Pat. 532,394 (Aug. 8, 1930), W. Lange.
37. W. Traube and A. Krahmer, *Chem. Ber.* **B52**, 1293 (1919).
38. Ger. Pats. 342,898 (Oct. 25, 1921), 346,245 (Dec. 27, 1921), W. Traube.
39. G. Olah, J. Nishimura, and Y. Mo., *Synthesis* **4**(11), 661 (1973).
40. U.S. Pats 3,254,107 (May 31, 1966), 3,255,228 and 3,255,229 (June 7, 1966), M. Hauptschein and M. Braid (to Pennsalt Chemicals Corp.); 3,083,220 (Mar. 26, 1963), E. L. Edens (to E. I. du Pont de Nemours & Co., Inc.); 2,878,156 (Mar. 17, 1959), R. A. Davis (to The Dow Chemical Co.); 2,628,927 (Feb. 17, 1953), J. D. Calfee and P. A. Florio (to Allied Chemical Corp.).
41. M. Hauptschein and M. Braid, *J. Am. Chem. Soc.* **83**, 2502 (1961).
42. W. V. Cicha and F. Aubke, *J. Am. Chem. Soc.* **111**(12), 4328–4331 (1989).
43. R. C. Paul, K. S. Dhindsa, *Proc. Indian Natl. Sci. Acad. Part A*, **47**(3), 357–372 (1981).
44. U.S. Pat. 1,847,513 (Mar. 1, 1932), W. Hentrich, M. Hardtmann, and H. Ossenbeck (to General Aniline Works).
45. W. Lange and E. Müller, *Chem. Ber.* **B63**, 2653 (1930).
46. J. P. Coleman and D. Pletcher, *Tetrahedron Lett.* (2), 147 (1974).
47. D. Pletcher and C. Smith, *Chem. Ind. (London)* **8**, 371 (1976).
48. W. Traube, *Chem. Ber.* **46**, 2525 (1913).
49. U.S. Pat. 2,312,413 (Mar. 2, 1943), R. K. Iler (to E. I. du Pont de Nemours & Co., Inc.).
50. U.S. Pats. 2,430,963 (Nov. 18, 1947), R. Stephenson and W. Watson (to Allied Chem. Corp.); U.S. Pat. 3,957,959 (May 18, 1976), R. Wheatley, D. Treadway, and R. Toennies (to E. I. du Pont de Nemours & CO., Inc.).
51. Jpn. Pat. 55126509 (Sept. 30, 1980), (to Akita Chem Co.).
52. V. I. D. Daritskii and co-workers, *Khim. Prom. (Moscow)*, (3) 183–184 (1991).
53. Br. Pat. 537,589 (June 27, 1941), (to Standard Oil Development Co.).
54. U.S. Pat. 2,313,103 (Mar. 9, 1943), C. L. Thomas (to Universal Oil Products Co.).
55. U.S. Pat. 3,778,489 (Dec. 11, 1973), P. T. Parker and I. Mayer (to Esso Research and Engineering Co.).
56. U.S. Pat. 3,922,319 (Nov. 25, 1975), J. W. Brockington (to Texaco, Inc.).
57. U.S. Pat. 3,928,487 (Dec. 23, 1975) D. A. McCauley (to Standard Oil Co.).
58. U.S. Pat. 4,008,178 (Feb. 15, 1977), J. W. Brockington (to Texaco, Inc.).
59. U.S. Pat. 2,428,279 (Sept. 3, 1947), V. N. Ipatieff and C. B. Linn (to Universal Oil Products Co.).
60. U.S. Pat. 2,421,946 (June 10, 1947), V. N. Ipatieff and C. B. Linn (to Universal Oil Products Co.).
61. U.S. Pat. 2,419,185 (Apr. 15, 1947), C. A. Braidwood and A. G. Hovey (to Reichold Chemicals).
62. U.S. Pat. 3,594,445 (July 20, 1971) P. T. Parker (to Esso Research and Engineering Co.).
63. U.S. Pat. 3,636,129 (Jan. 18, 1972), (to Esso Research and Engineering Co.).
64. U.S. Pat. 3,678,120 (July 18, 1972), H. S. Bloch (to Universal Oil Products Co.).
65. U.S. Pat. 3,708,553 (Jan. 2, 1973), G. A. Olah (to Esso Research and Engineering Co.).
66. D. T. Roberts, Jr. and L. E. Calihan, *J. Macromol. Sci. Chem.* **7**, 1629 (1973).
67. U.S. Pat. 3,819,743 (June 25, 1974), D. A. McCauley (to Standard Oil Co.).

68. U.S. Pat. 3,925,495 (Dec. 9, 1975), P. G. Rodewald (to Mobil Oil Corp.).
69. U.S. Pat. 3,984,352 (Oct. 5, 1976), P. G. Rodewald (to Mobil Oil Corp.).
70. U.S. Pat. 5,081,318 (Mar. 4, 1991), J. F. Knifton (to Texaco).
71. G. A. Olah and co-workers, *J. Org. Chem.* **56**(21) 6148–6151 (1991).
72. Jpn. Pat. 01075442 A2 (Mar. 22, 1989), Y. Sama (to Agency of Industrial Science and Technology).
73. U.S. Pat. 4,544,774 (Oct. 1, 1985), R. Pick (to Du Pont).
74. U.S. Pat. 4,569,990 (Feb. 11, 1986), W. W. Kasper and co-workers (to Du Pont).
75. Can. Pat. 448,662 (May 25, 1948), A. C. Hopkins, Jr., R. M. Stephenson, and W. E. Watson (to Allied Chemical Corp.).
76. Brit. Pat. 755,692 (Aug. 22, 1956), A. J. Edwards (to National Smelting Co., Ltd.).
77. W. Traube, J. Horenz, and F. Wunderlich, *Chem. Ber.* **B52**, 1272 (1919).
78. W. Traube and E. Brehmer, *Chem. Ber.* **B52**, 1284 (1919).
79. U.S. Pat. 2,428,753 (Oct. 7, 1947), C. B. Linn (to Universal Oil Product Co.).
80. U.S. Pat. 2,434,040 (Jan. 6, 1948), B. F. Hartman (to Socony-Vacuum Oil Co.).
81. Brit. Pat. 824,427 (Dec. 2, 1959), H. R. Leech and W. H. Wilson (to Imperial Chemical Industries, Ltd.).
82. C. B. F. Young and K. R. Hesse, *Met. Finish.* **45**(2), 63, 84 (1947); C. B. F. Young and K. R. Hesse, *Met. Finish.* **45**(3), 64 (1947).
83. Ger. Pat. DE 3438433 A1 (May 15, 1985), (to Mitsubishi Heavy Ind. Ltd.).
84. A. Kaiser, *Glastech Ber.* **62**(4) 127–134 (1989).
85. R. C. Paul and co-workers, *J. Inorg. Nucl. Chem.* **34**, 2535 (1972).
86. D. D. Des Marteau and M. Eisenberg, *Inorg. Chem.* **11**, 2641 (1972).
87. F. B. Dudley and G. H. Cady, *J. Am. Chem. Soc.* **79**, 513 (1957).
88. *Ibid.* **85**, 3375 (1963).
89. F. Aubke and D. D. Des Marteau, *Fluorine Chem. Rev.* **8**, 74 (1977).
90. R. A. DeMarco and J. M. Shreeve, *Adv. Inorg. Chem. Radiochem.* **16**, 115 (1974).
91. J. E. Roberts and G. H. Cady, *J. Am. Chem. Soc.* **81**, 4166 (1959).
92. *Ibid.* **82**, 352 (1960).
93. R. Seeley and A. W. Jache, *J. Fluorine Chem.* **2**(3), 225 (1973).

FRANCIS E. EVANS
GANPAT MANI
AlliedSignal Inc.

Related Articles

Fluorine Compounds, Inorganic, Sulfur