*Kirk-Othmer Encyclopedia of Chemical Technology.*

# FLUORINE COMPOUNDS, INORGANIC, NITROGEN

Nitrogen has four binary fluorides: nitrogen trifluoride [7783-54-2], $NF_3$; tetrafluorohydrazine [10036-47-2], $N_2F_4$; difluorodiazine [10578-16-2], $N_2F_2$; and fluorine azide [14986-60-8], $FN_3$. There are numerous other nitrogen fluorine compounds, the most significant of which are the perfluoroammonium salts based on the $NF^+{}_4$ cation. Of all the nitrogen fluorine compounds, only $NF_3$ has been of commercial importance. Nitrogen trifluoride is used as an etchant gas in the electronics industry and as a fluorine source in high power chemical lasers.

## 1. Nitrogen Trifluoride

### 1.1. Physical Properties

Nitrogen trifluoride, $NF_3$, is a colorless gas, liquefying at 101.3 kPa (1 atm) and $-129.0^\circ C$, and solidifying at $-206.8^\circ C$ (1). High purity $NF_3$ has little odor, but material contaminated with traces of active fluorides may have a pungent, musty odor. $NF_3$, a pyramidal molecule with $C_{3v}$ point group symmetry, has a structure similar to ammonia. The N–F bonds are 0.137 nm and the F–N–F bond makes a 102.1° angle. Selected physical properties of $NF_3$ are given in Table 1. An extensive tabulation and correlation of all the physical properties of $NF_3$ is available (2). The infrared (3), Raman (4), and ultraviolet spectra (5) of $NF_3$ have been investigated.

### 1.2. Chemical Properties

$NF_3$ can be a potent oxidizer, especially at elevated temperature. At temperatures up to ca 200°C, its reactivity is comparable to oxygen. At higher temperatures, the homolysis of the N–F bond into $NF_2$ and F free radicals becomes significant. The F radical reacts with organic compounds and certain metals, liberating heat and causing further dissociation of the $NF_3$. At temperatures above 400°C, the reactivity of $NF_3$ becomes more like that of fluorine. The thermal dissociation of $NF_3$ has been studied by a number of investigators (11–14) and was found to peak in the temperature range of 800 to 1200°C.

Nitrogen trifluoride acts primarily upon the elements as a fluorinating agent, but is not a very active one at lower temperatures. At elevated temperatures, $NF_3$ pyrolyzes with many of the elements to produce $N_2F_4$ and the corresponding fluoride. The element used in this reaction scavanges the fluorine radical, allowing the $NF_2$ radicals to combine. The pyrolysis of $NF_3$ over copper turnings produces $N_2F_4$ in a 62–71% yield at 375°C (15). Pyrolysis over carbon at 400–500°C is more favorable (16, 17). This process was the basis for the commercial production of $N_2F_4$ in the early 1960s for use in rocketry.

Hydrogen and hydrides react with $NF_3$ with the rapid liberation of large amounts of heat. This is the basis for the use of $NF_3$ in high energy chemical lasers (qv). The flammability range of $NF_3$–$H_2$ mixtures is 9.4–95 mol % $NF_3$ (17), whereas the flammability range of $NF_3$–$SiH_4$ mixtures is even broader at 4.7–99.34 mol % $NF_3$ (18). Nitrogen trifluoride reacts with organic compounds but generally an elevated temperature

**Table 1. Physical Properties of Nitrogen Trifluoride**

| Property | Value | Reference |
|---|---|---|
| boiling point, °C | −129.0 | 1 |
| liquid density at −129°C, g/mL | 1.533 | 6 |
| heat of vaporization, kJ/mol[a] | 11.59 | 1 |
| triple point, °C, 0.263 Pa[b] | −206.8 | 7 |
| heat of fusion, J/mol[a] | 398 | 1 |
| solid transition point, °C | −216.5 | 2 |
| heat of transition, kJ/mol[a] | 1.513 | 2 |
| critical temperature, °C | −39.25 | 6 |
| critical pressure, kPa[b] | 4530 (44.7 atm) | 6 |
| critical volume, $cm^3$/mol | 123.8 | 8 |
| heat of formation, kJ/mol[a] | −131.5 | 9 |
| heat capacity at 25°C, J/(mol·K)[a] | 53.39 | 9 |
| water solubility, 101.3 kPa,[b] 25°C | $1.4 \times 10^{-5}$ mol $NF_3$/mol $H_2O$ | 10 |
| vapor pressure equation, $P$ in kPa[c] | $\log P = 5.90445 - \frac{501.913}{T - 15.37}$ | 6 |

[a] To convert kJ to kcal, divide by 4.184.

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

[c] For $P$ in mm Hg, $\log P = 6.77966 - \frac{501.913}{T - 15.37}$

is required to initiate the reaction. Under these conditions, the reaction often proceeds explosively and great care must be exercised when exposing $NF_3$ to organic compounds. Therefore, $NF_3$ has found little use as a fluorinating agent for organic compounds. The reactions of $NF_3$ with the elements, and various inorganic and organic substances, are summarized in Reference 2.

Although $NF_3$ is an amine, it exhibits virtually no basic properties and is not protonated by the $HSO_3F$–$SbF_5$–$SO_3$ superacid medium at 20°C (19). Commercial scrubbing systems for unwanted $NF_3$ are available (20) and work on the principle of pyrolysis of the $NF_3$ over reactive substrates at high temperatures.

$NF_3$ reacts with $F_2$ and certain Lewis acids under heat or uv light to form the corresponding $NF^+{}_4$ salts. For example, when $NF_3$, $SbF_5$, and $F_2$ are mixed in a 1:1:1.5 ratio in a Monel vessel and heated to 200°C for 50 hours, a 41% yield of $NF_4SbF_6$ [16871-76-4] is obtained (21). $NF^+{}_4$ salts had been thought to be too unstable to be synthesized (22). Preparation methods have been described which use other sources of energy to initiate the reaction. $NF_4AsF_6$ [16871-75-3] (23) and $NF_4BF_4$ [15640-93-4] (24) were prepared using a low temperature glow discharge. $NF_4PF_6$ [58702-88-8] and $NF_4GeF_5$ [58702-86-6] were prepared by uv photolysis (25). This series of compounds has been further extended by metathesis between $NF_4SbF_6$ and other salts in HF solution. For example, $(NF_4)_2TiF_6$ [61128-92-5] was prepared by the metathesis of $Cs_2TiF_6$ and $NF_4SbF_6$ in HF (26).

The salts rapidly hydrolyze to form $NF_3$ and $O_2$, and react with glass at temperatures above 85°C to form $NF_3$ and $SiF_4$ (21). The $NF^+{}_4$ salts are stable in dry atmospheres to 200°C, but rapidly decompose above 300°C to yield $NF_3$, $F_2$, and the corresponding Lewis acid. Therefore, these salts are solid sources of $NF_3$ and $F_2$, free of atmospheric contaminants and HF.

### 1.3. Manufacture and Economics

Nitrogen trifluoride can be formed from a wide variety of chemical reactions. Only two processes have been technically and economically feasible for large-scale production: the electrolysis of molten ammonium acid fluoride; and the direct fluorination of the ammonia in the presence of molten ammonium fluoride. In the electrolytic process, $NF_3$ is produced at the anode and $H_2$ is produced at the cathode. In a divided cell of 4 kA

**Table 2. Specifications of $NF_3$[a]**

| Impurity | Commercial, ppmv | VLSI, ppmv | Megaclass, ppmv |
|---|---|---|---|
| total fluorides as HF | 3,900 | 1 | 1 |
| $CO_2$ | 130 | 16 | 4 |
| CO | 330 | 25 | 0.5 |
| $CF_4$ | 1,200 | 560 | 25 |
| $N_2$ | 19,000 | 130 | 10 |
| $O_2$ + Ar | 22,000 | 100 | 6 |
| $SF_6$ | 50 | 25 | 1 |
| $N_2O$ | 500 | 16 | 2 |
| $H_2O$ | 1 | 1 | 1 |

[a] Commercial grades offered by Air Products and Chemicals, Inc.

having nickel anodes, extensive dilution of the gas streams with $N_2$ was used to prevent explosive reactions between $NF_3$ and $H_2$ (17).

In the direct process, $NF_3$ is produced by the reaction of $NH_3$ and $F_2$ in the presence of molten ammonium acid fluoride (27). The process uses a specially designed reactor (28). Because $H_2$ is not generated in this process, the hazards associated with the reactions between $NF_3$ and $H_2$ are eliminated.

As a result of the development of electronic applications for $NF_3$, higher purities of $NF_3$ have been required, and considerable work has been done to improve the existing manufacturing and purification processes (29). $N_2F_2$ is removed by pyrolysis over heated metal (30) or metal fluoride (31). This purification step is carried out at temperatures between 200–300°C which is below the temperature at which $NF_3$ is converted to $N_2F_4$. Moisture, $N_2O$, and $CO_2$ are removed by adsorption on zeolites (29, 32). The removal of $CF_4$ from $NF_3$, a particularly difficult separation owing to the similar physical and chemical properties of these two compounds, has been described (33, 34).

Production of $NF_3$ is less than 100 t/yr in the United States. Air Products and Chemicals, Inc. is the only commercial producer in the United States. The 1992 price ranged from \$400–\$800/kg depending on the grade.

### 1.4. Specifications and Analysis

Nitrogen trifluoride is shipped as a high pressure gas at 10 MPa (1450 psig) and is available in tube trailers and cylinders. Table 2 shows $NF_3$ specifications for a commercial grade typically used in chemical laser applications, and two higher grades of $NF_3$ used by the electronics industry. Analysis of $NF_3$ for impurities can be performed on the gas chromatograph (35). Active fluorides are determined by scrubbing with a basic solution and wet-chemical analysis for fluoride content (35).

### 1.5. Handling and Toxicity

Nitrogen trifluoride gas is noncorrosive to the common metals at temperatures below 70°C and can be used with steel, stainless steel, and nickel. The corrosion rate of $NF_3$ on these materials significantly increases with moisture or HF. Nitrogen trifluoride is compatible with the fluorinated polymers such as Teflon, Kel-F, and Viton at ambient conditions. Extensive data on the corrosion rates of gaseous and liquid $NF_3$ to a variety of metals and nonmetals are compiled in Reference 2. In systems handling high pressure $NF_3$, precautions should be taken to avoid any sudden heating of the $NF_3$ which can occur during adiabatic compression of the gas during the introduction of $NF_3$ rapidly from a high pressure point to a low pressure dead-end space (20).

Nitrogen trifluoride is a toxic substance and is most hazardous by inhalation. $NF_3$ induces the production of methemoglobin which reduces the level of oxygen transfer to the body tissues. At the cessation of $NF_3$

exposure methemoglobin reverts back to hemoglobin. The OSHA permissible exposure limits is set as a TLV–TWA of 29 mg/kg or 10 ppm (36). Because $NF_3$ has very little odor, it cannot be detected by its odor at concentrations within the TLV. Therefore, adequate personnel protection or monitoring must be provided when handling $NF_3$. Commercially available monitors detect $NF_3$ by either pyrolysis to HF or $NO_2$ followed by electrochemical quantification, or by infrared absorption (20). All of the monitors can detect at least 1 ppm or 10 times below the TLV. The pyrolysis–electrolytic monitors are generally less expensive, but other halogen-containing compounds can interfere with the $NF_3$ detection.

The inhalation toxicity of $NF_3$ on animals has been studied extensively (37–40). These studies provide the basis of emergency exposure limits (EEL) that have been proposed for $NF_3$. The NAS–NRC Committee on Toxicology recommends that the EEL for $NF_3$ be 10 min at 2250 ppm, 30 min at 750 ppm, and 60 min at 375 ppm. Gaseous $NF_3$ is considered to be innocuous to the skin and a minor irritant to the eyes and mucous membranes. $NF_3$ does give a weakly positive metabolically activated Ames test but only at concentrations greater than 2% or 10 times the 10 minute EEL.

Environmental impact studies on $NF_3$ have been performed. Although undiluted $NF_3$ inhibits seed growth, no effect on plant growth was observed when exposed to $6,000$ ppm·min of $NF_3$ and only minor effects were observed at the $60,000$ ppm·min exposure level (41). Exposure of microbial populations to 25% $NF_3$ in air for seven hours showed normal growth. $NF_3$ is not an ozone-depleting gas (20).

### 1.6. Uses

The principal use of $NF_3$ is as a fluorine source in the electronics industry. The use of $NF_3$ as a dry chemical etchant has been reviewed (20, 42–44). The advantages of using $NF_3$ as an etchant over traditional carbon-based etchants include high etch rates, high selectivities for nitride-over-oxide etching and single-crystal silicon over thermally grown oxide, and the production of only volatile reaction products resulting in an etch with no polymer or fluoride residues. *In situ* plasma or thermal cleaning of chemical vapor deposition (CVD) reactors is also a use of $NF_3$. Residual coatings are deposited on the internal surfaces of CVD reactors during deposition processes. A plasma of $NF_3$ can remove these deposits as volatile fluorides in minutes at the process temperature eliminating the need to remove the internal CVD reactor components to be cleaned by acid tank immersion.

Another use of $NF_3$ is as a fluorine source for the hydrogen and deuterium fluoride (HF/DF) high energy chemical lasers(qv). The HF/DF lasers are the most promising of the chemical lasers under development because a substantial fraction (ca 25%) of the energy of the reaction between $H_2/D_2$ and $F_2$ can be released as laser radiation (45, 46). The use of $NF_3$ is preferred to $F_2$ because of its comparative ease of handling at ambient temperatures. Storage and handling of $NF_3$ do not require the precautions necessary for the large-scale use of fluorine.

## BIBLIOGRAPHY

"Nitrogen Trifluoride" under "Fluorine Compounds, Inorganic" in *ECT* 1st ed., Vol. 6, p. 710; "Nitrogen" under "Fluorine Compounds, Inorganic" in *ECT* 2nd ed., Vol. 9, pp. 629–630 by W. E. White, Ozark-Mahoning Co.; in *ECT* 3rd ed., Vol. 10, pp. 768–772, by A. J. Woytek, Air Products and Chemicals, Inc.

### Cited Publications

1. L. Pierce and E. L. Pace, *J. Chem. Phys.* **23**, 551 (1955).
2. R. E. Anderson, E. M. Vander Wall, and R. K. Schaplowsky, "Nitrogen Trifluoride," *USAF Propellant Handbook*, AFRPL-TR-77-71, Contract F04611-76-C-0058, Aerojet Liquid Rocket Co., Sacramento, Calif., 1977.

3. P. N. Schatz and I. W. Levin, *J. Chem. Phys.* **29**, 475 (1958).
4. M. Gilbert, P. Nectoux, and M. Drifford, *J. Chem. Phys.* **68**, 679 (1978).
5. V. Legasov and co-workers, *J. Fluorine Chem.* **11**(2), 109 (1978).
6. R. L. Jarry and H. C. Miller, *J. Phys. Chem.* **60**, 1412 (1956).
7. *DIPPR on-line database on STN*, American Institute of Chemical Engineers, New York, 1992.
8. D. N. Seshadri, D. S. Viswanath, and N. R. Kuloor, *Indian J. Technol.* **8**(5), 153 (1970).
9. D. Wagman and co-workers, *J. Phys. Chem. Ref. Data*, Suppl. No. 2 (1982).
10. C. R. S. Dean, A. Finch, and P. J. Gardner, *J. Chem. Soc., Dalton Trans.* **23**, 2722 (1973).
11. K. O. McFadden and E. Tschuikow, *J. Phys. Chem.* **77**, 1475 (1973).
12. G. L. Schott, L. S. Blair, and J. D. Morgan, Jr., *J. Phys. Chem.* **77**, 2823 (1973).
13. E. A. Karko and co-workers, *J. Chem. Phys.* **63**, 3596 (1975).
14. P. J. Evans and E. Tschuikow-Roux, *J. Chem. Phys.* **65**, 4202 (1976).
15. C. B. Colburn and A. Kennedy, *J. Am. Chem. Soc.* **80**, 5004 (1958).
16. *Chem. Eng. News* **38**, 85 (Sept. 19, 1960).
17. U.S. Pat. 3,235,474 (Feb. 15, 1966), J. F. Tompkins (to Air Products and Chemicals, Inc.).
18. Y. Urano, K. Tokuhashi, S. Kondo, S. Horiguchi, and M. Iwsaka, *20th Safety Engineering Symposium*, Tokyo, Japan, June 1990.
19. R. J. Gillespie and G. P. Pez, *Inorg. Chem.* **8**, 1233 (1969).
20. *Nitrogen Trifluoride: Safety, Applications, and Technical Data Manual*, Air Products and Chemicals, Inc., Allentown, Pa., 1992.
21. W. E. Tolberg and co-workers, *Inorg. Chem.* **6**, 1156 (1967).
22. W. C. Price, T. R. Passmore, and D. M. Roessler, *Discussions Faraday Soc.* **35**, 201 (1963).
23. J. P. Guertin, K. O. Christie, and A. E. Pavlath, *Inorg. Chem.* **5**, 1921 (1966).
24. S. M. Sinel'nikov and V. Ya. Rosolovskii, *Dokl. Akad. Nauk SSSR* **194**, 1341 (1970).
25. K. O. Christie, C. J. Schack, and R. D. Wilson, *Inorg. Chem.* **15**, 1275 (1976).
26. K. O. Christie and C. J. Schack, *Inorg. Chem.* **16**, 353 (1977).
27. U.S. Pat. 4,091,081 (May 23, 1978), A. J. Woytek and J. T. Lileck (to Air Products and Chemicals, Inc.).
28. *Chem. Eng.* **84**(26), 116 (1977).
29. A. J. Woytek and P. B. Henderson, in A. J. Woytek and P. B. Henderson, *Proceedings of the Institute of Environmental Sciences 37th Annual Meeting*, IES, Mount Prospect, Ill., 1990, p. 570.
30. U.S. Pat. 4,193,976 (Mar. 18, 1980), J. T. Lileck, J. Papinsick, and E. J. Steigerwalt (to Air Products and Chemicals, Inc.).
31. U.S. Pat. 4,948,571 (Dec. 3, 1988), I. Harada, H. Hokonohara, and T. Yamaguchi (to Mitsui Toatsu Chemicals, Inc.).
32. Eur. Pat. Appl. 366 078 A2 , (May 2, 1990), M. Aritsuka and N. Iwanaga (to Mitsui Toatsu Chemicals, Inc.).
33. U.S. Pat. 5,069,690 (Dec. 3, 1991), P. B. Henderson, C. G. Coe, D. E. Fowler, and M. S. Benson (to Air Products and Chemicals, Inc.).
34. U.S. Pat. 5,069,887 (Dec. 3, 1991), T. Suenaga, T. Fujii, and Y. Kobayashi (to Central Glass).
35. L. A. Dee, *Analysis of Nitrogen Trifluoride*, AFRPL-TR-76-20 (AD-A022887), Air Force Rocket Propulsion Laboratory, Edward Air Force Base, Calif., Apr. 1976.
36. J. O. Accrocco and M. Cinquanti, eds., *Right-To-Know Pocket Guide for Laboratory Employees*, Genium, Schenectady, N.Y., 1990.
37. E. H. Vernot and C. C. Haun, *Acute Toxicology and Proposed Emergency Exposure Limits of Nitrogen Trifluoride*, AMRL-TR-69-130-Paper No. 13 (AD 710062), Contract F33615-70-V-1046, Syste-Med Corp., Dayton, Ohio, Dec. 1969. Reprinted from the *Proceedings of the 5th Annual Conference on Atmospheric Contamination in Conhned Spaces, Sept. 16–18, 1969*, AMRL-TR-69-130 (AD 709994), Dayton, Ohio, Dec. 1969, 165–171.
38. F. N. Dost and co-workers, "*Metabolism and Pharmacology of Inorganic and Fluorine Containing Compounds*," *Final Report (July 1, 1964–June 30, 1967)*, AMRL-TR-67-224 (AD 681-161), Contract AF 33(615)-1799, Oregon State University, Corvallis, Oreg., Aug. 1968.
39. F. N. Dost, D. J. Reed, and C. H. Wang, *Toxicol. Appl. Pharmacol.* **17**, 585 (1970).
40. G. L. Coppoc and S. J. Leger, "Effect of Nitrogen Trifluoride on Plasma Concentrations of Lactate, Methemoglobin, and Selected Enzymes," *ApriWune 1968*, SAM-TR-70-42 (AD 711044), School of Aerospace Medicine, Brooks Air Force Base, Texas, July 1970.

41. D. J. Reed, F. N. Dost, and C. H. Want, "Inorganic Fluoride Propellant Oxidizers, Vol. 1: Their Effects Upon Seed Germination and Plant Growth," *Interim Report (May 15, 1964–May 15, 1966)*, AMRLTR-66-187, Vol. I (AD 667-556), Contract AF 33(615)-1767, Oregon State University, Corvallis, Oreg., Nov. 1967.
42. A. J. Woytek, J. T. Lileck, and J. A. Barkanic, *Solid State Technol.* **27**, 109 (1979).
43. J. A. Barkanic and co-workers, *Solid State Technol.* **32**, 172 (1984).
44. J. M. Parks, R. J. Jaccodine, J. G. Langan, and M. A. George, in *Proceedings of the 8th Symposium on Plasma Processing*, Electrochemical Society, Montreal, Canada, May 6, 1990, p. 701.
45. E. R. Schulman, W. G. Burwell, and R. A. Meinzer, "Design and Operation of Medium Power CW HF/DF Chemical Lasers," *AIAA 7th Fluid and Plasma Dynamics Conference*, Palo Alto, Calif., AIAA Paper No. 74-546, June 1974.
46. P. J. Klass, *Aviat. Week Space Technol.* **107**, 34 (Aug. 1976).

### General Reference

47. C. J. Hoffman and R. G. Neville, *Chem. Reo.* **62**, 1 (1962); A. W. Jache and W. E. Shite, in C. A. Hunpel, ed., *Encyclopedia of Electrochemistry*, Reinhold Publishing Corp., New York, 1964, 856–859; R. E. Anderson, E. M. Vander Wall, and R. K. Schaplowsky, "Nitrogen Trifluoride," *USAF Propellant Handbook*, AFRPL-TR-77-71, Contract F0461 1-76-C-0058, Aerojet Liquid Rocket Co., Sacramento, Calif., 1977.

PHILIP B. HENDERSON
ANDREW J. WOYTEK
Air Products and Chemicals, Inc.

## Related Articles

Fluorine Compounds, Inorganic, Introduction; Fluorine Compounds, Inorganic, Aluminum; Fluorine Compounds, Inorganic, Ammonium; Fluorine Compounds, Inorganic, Antimony; Fluorine Compounds, Inorganic, Arsenic; Fluorine Compounds, Inorganic, Barium; Fluorine Compounds, Inorganic, Calcium; Fluorine Compounds, Inorganic, Cobalt; Fluorine Compounds, Inorganic, Copper; Fluorine Compounds, Inorganic, Germanium; Fluorine Compounds, Inorganic, Halogens; Fluorine Compounds, Inorganic, Hydrogen; Fluorine Compounds, Inorganic, Iron; Fluorine Compounds, Inorganic, Lead; Fluorine Compounds, Inorganic, Lithium; Fluorine Compounds, Inorganic, Magnesium; Fluorine Compounds, Inorganic, Mercury; Fluorine Compounds, Inorganic, Molybdenum; Fluorine Compounds, Inorganic, Nickel; Fluorine Compounds, Inorganic, Oxygen; Fluorine Compounds, Inorganic, Phosphorus; Fluorine Compounds, Inorganic, Potassium; Fluorine Compounds, Inorganic, Rhenium; Fluorine Compounds, Inorganic, Silver; Fluorine Compounds, Inorganic, Sodium; Fluorine Compounds, Inorganic, Tantalum; Fluorine Compounds, Inorganic, Tin; Fluorine Compounds, Inorganic, Titanium; Fluorine Compounds, Inorganic, Tungsten; Fluorine Compounds, Inorganic, Zinc; Fluorine Compounds, Inorganic, Zirconium