HALOGEN FLUORIDES

1. Introduction

The halogen fluorides are binary compounds of bromine, chlorine, and iodine with fluorine. Of the eight known compounds, only bromine trifluoride, chlorine trifluoride, and iodine pentafluoride have been of commercial importance. Properties and applications have been reviewed (1–7) as have the reactions with organic compounds (8). Reviews covering the methods of preparation, properties, and analytical chemistry of the halogen fluorides are also available (9).

The halogen fluorides are best prepared by the reaction of fluorine with the corresponding halogen. These compounds are powerful oxidizing agents; chlorine trifluoride approaches the reactivity of fluorine. In descending order of reactivity the halogen fluorides are chlorine pentafluoride [13637-63-3], ClF_5; chlorine trifluoride [7790-91-2], ClF_3; bromine pentafluoride [7789-30-2], BrF_5; iodine heptafluoride [16921-96-3], IF_7; chlorine monofluoride [7790-91-2], ClF; bromine trifluoride [7787-71-5], BrF_3; iodine pentafluoride [7783-66-6], IF_5; and bromine monofluoride [13863-59-7], BrF.

The halogen fluorides offer an advantage over fluorine in that the former can be stored as liquids in steel containers and, unlike fluorine, high pressure is not required. Bromine trifluoride is used as an oxidizing agent in cutting tools used in deep oil-well drilling, whereas chlorine trifluoride is used to convert uranium to UF_6 in nuclear fuel processing (see PETROLEUM).

Except for iodine pentafluoride, the halogen fluorides have no commercial importance as fluorinating agents. Their extreme reactivity and the accompanying energy release of the reaction can be sufficient to disrupt C—C bonds and can result in explosive reactions or fires. In addition, both halogens are generally then introduced into organic compounds, giving rise to a complex mixture of products.

2. Physical Properties

The physical properties of the halogen fluorides are given in Table 1. Calculated thermodynamic properties can be found in Reference 24.

2.1. Bromine Monofluoride. Bromine monofluoride is red to red-brown (4) and is unstable, disproportionating rapidly into bromine and higher fluorides. Therefore, the measurement of its physical properties is difficult and the values reported in Table 1 are only approximate. The uv-absorption spectrum is available (25).

2.2. Bromine Trifluoride. Bromine trifluoride is a colorless liquid. The commercial grade is usually amber to red because of slight bromine contamination. The molecule has a distorted T structure (26). Infrared spectral data (26–30), the uv-absorption spectrum (31), and vapor pressure data (32) may be found in the literature.

2.3. Bromine Pentafluoride. Bromine pentafluoride is a colorless liquid having the molecular structure of a tetragonal pyramid (5). The index of refraction n_D is 1.3529 (33). Infrared spectra (13,34), the uv-absorption spectrum (35), and vapor pressure data (11) are all available.

2.4. Chlorine Monofluoride. Chlorine monofluoride is a colorless gas that condenses to a liquid with a slight yellow cast and freezes to a white solid. The infrared spectrum of gaseous chlorine monofluoride and the Raman spectrum of the liquid have been studied (36). The uv-absorption spectrum (37) and vapor pressure data are also available (11).

An equilibrium exists between chlorine trifluoride, chlorine monofluoride, and fluorine gas (38). The equilibrium constant may be expressed as

$$K_p = \frac{(P_{ClF})(P_{F_2})}{(P_{ClF_3})}$$

where P_X is the partial pressure of substance X. Values for K_p are

Temperature, °C	Pa (mm Hg)
250	30 (0.22)
300	240 (1.8)
350	1450 (10.9)

2.5. Chlorine Trifluoride. Chlorine trifluoride is a pale yellow liquid or a colorless gas. It freezes to a white solid and undergoes a transition in the solid state at −82.66°C (11). The infrared and Raman spectra have been studied (28,29,39,40) as has the uv absorption spectrum (41). Vapor pressure data are given in Reference 42. The viscosity of the liquid is 0.448 mPa · s(=cP) at 290 K, and the surface tension is 26.6 mN/m(=dyn/cm) at 273 K (43). The density of the solid is 2.530 g/cm^3 at 153 K (44). The vapors of chlorine trifluoride are nonideal and this has been attributed to the following equilibrium:

$$2\,ClF_3 \rightleftharpoons Cl_2F_6$$

Table 1. **Physical Properties of the Halogen Fluorides**[a]

Property	BrF	BrF_3	BrF_5	ClF	ClF_3	ClF_5	IF_5	IF_7
boiling point, °C	20	125.7	40.9	−100.1	11.75	−13.1	102	5.5
melting point, °C	−33	8.8	−60.6	−155.6	−76.3	−103	8.5	4.5
liquid density at 25°C, g/mL		2.803	2.463[b]	1.620[b]	1.825[b]	1.790[c]	3.252	2.669
critical temperature, °C					154.5	142.6		
$-\Delta H_f$ (g) at 25°C, kJ/mol[d]	58.5	255.4	443.9	56.4	164.5	254.6	839.3	961.0
$-\Delta G_f$ (g) at 25°C, kJ/mol[d]	73.6	229.1	351.5	57.7	124.4	163.0	771.6	841.4
heat of vaporization, kJ/mol[d]		42.8	30.6	20.1	27.50	22.21	35.92	24.7
E_{diss}, kJ/mol[d]	254 260			253	105 160			122
heat of fusion, kJ/mol[d]		12.01	5.66		7.60		11.21	
specific heat, gas, J/(mol · K)[d]	32.9	66.5[e]		32.0	65.2		99.1	136.3
specific conductivity, liquid, at 25°C, W · cm		8.0×10^{-3}	9.1×10^{-8}	1.9×10^{-7}[f]	4.9×10^{-9}	1.25×10^{-9}[g]	5.4×10^{-6}	10^{-9}

[a] Compiled from References 8,10–23.

[b] At boiling point.

[c] At 20°C.

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

[e] The specific heat of the liquid is 124.5J/(mol · K) (29.8cal/(mol · K)).

[f] At 145 K.

[g] At 256 K.

The equilibrium constant at 24.2°C is 2.84 kPa (21.3 mm Hg) (11):

$$K_p = \frac{P_{Cl_2F_6}}{(P_{ClF_3})^2}$$

2.6. Chlorine Pentafluoride. Chlorine pentafluoride is a colorless gas at room temperature. The ir and Raman spectra of the liquid and gas phase have been studied (34,39). The uv absorption spectrum (45) and vapor pressure data may be found in the literature (18).

2.7. Iodine Pentafluoride. Iodine pentafluoride is a straw-colored liquid; the ir and Raman spectra of the gas phase have been studied (19,46,47); vapor pressure data are given in References 14 and 48.

2.8. Iodine Heptafluoride. Iodine heptafluoride is a colorless liquid; the ir and Raman spectra of the gas have been studied (47,49); vapor pressure data are available (19).

3. Chemical Properties

3.1. Reactions with Metals. All metals react to some extent with the halogen fluorides, although several react only superficially to form an adherent fluoride film of low permeability that serves as protection against further reaction. This protective capacity is lost at elevated temperatures, however. Hence, each metal has a temperature above which it continues to react. Mild steel reacts rapidly above 250°C. Copper and nickel lose the ability to resist reaction above 400 and 750°C, respectively.

Metals that form no protective fluoride film react readily with the halogen fluorides. Chlorine trifluoride reacts with Hg, As, Ca, Ti, Co, Pt, and Pb at elevated temperatures to give HgF_2, AsF_5, CaF_2, TiF_3, CoF_3, PtF_5, and PbF_{3-4}, respectively (50). Titanium alloys and molybdenum alloys and niobium metal react vigorously with ClF_3 (51). Molybdenum and tungsten react with BrF_3 to form the volatile MoF_6 and WF_6 (52,53). Chlorine trifluoride (54) converts Nb and Ta to pentafluorides, and Mo and Re to hexafluorides.

Uranium is converted by ClF_3, BrF_3, and BrF_5 to UF_6. The recovery of uranium from irradiated fuels has been the subject of numerous and extensive investigations sponsored by atomic energy agencies in a number of countries (55–63). The fluorides of the nuclear fission products are nonvolatile; hence the volatile UF_6 can be removed by distillation (see NUCLEAR REACTORS; URANIUM AND URANIUM COMPOUNDS).

The rapid reaction of ClF_3 and BrF_3 with metals is the basis of the commercial use in cutting pipe in deep oilwells (64–68). In this application, the pipe is cut by the high temperature reaction of the halogen fluoride and the metal.

3.2. Reactions with Nonmetals. Few elements withstand the action of interhalogen compounds at elevated temperatures and many react violently at or below ambient temperatures. The oxidation of the element proceeds to its highest valence state, whereas the halogen other than fluorine is reduced either to the element or a lower valent interhalogen derivative. The oxidizing capacity of the interhalogens varies substantially from compound to compound. For example, chlorine trifluoride reacts vigorously with virtually every element at room temperature; on the other hand, iodine pentafluoride has a much milder oxidizing power. Thus chlorine trifluoride oxidizes xenon to xenon fluorides whereas iodine pentafluoride does not react (11). Furthermore, all stable halogen fluorides, except iodine pentafluoride, oxidize radon between −195 and 25°C (69) (see HELIUM-GROUP GASES, COMPOUNDS).

In general, reactions of halogens and halogen fluorides yield mixtures (4). Bromine pentafluoride reacts with iodine at ambient temperatures and with chlorine at 250–300°C, giving mixtures of interhalogen compounds. Bromine pentafluoride has been stored with bromine in steel cylinders at room temperature for extended periods of time without appreciable reaction. At elevated temperatures BrF_3 is formed. Bromine and chlorine trifluoride give bromine trifluoride (60–80% yields) and chlorine (70). Iodine and chlorine trifluoride produce IF_5 and ICl (70). Chlorine reacts with chlorine trifluoride to produce chlorine monofluoride. Bromine and iodine react with chlorine monofluoride to produce BrF_3 and IF_5, respectively. Bromine reacts with IF_5 on warming to give IBr and BrF_3 (4). Chlorine reacts with IF_7 to give ClF and interhalogens of iodine and chlorine (4).

Halogen fluorides react with sulfur, selenium, tellurium, phosphorus, silicon, and boron at room temperature to form the corresponding fluorides. Slight warming may be needed to initiate the reactions (4) which, once started, proceed rapidly to completion accompanied by heat and light. The lack of protective film formation allows complete reaction.

3.3. Reactions with Inorganic Compounds. In an investigation of the reactions of BrF_3 with oxides (71–73), little or no reaction was found with the oxides of Be, Mg, Ce, Ca, Fe, Zn, Zr, Cd, Sn, Hg, Th, and the rare earths, whereas the oxides of Mo and Re formed stable oxyfluorides. Manganese dioxide reacted incompletely but $KMnO_4$ released oxygen quantitatively. Complete replacement of oxygen took place with oxides of B, Ti, V, Cr, Cu, Ge, As, Se, Nb, Sb, Te, I, Ta, W, Tl, Pb, Bi, and U at 75°C.

Oxygen was partially replaced when P_2O_5, V_2O_5, and CrO_3 were dissolved in IF_5 to form POF_3, VOF_3, and CrO_2F_2. With WO_3 and MoO_3, $WO_3 \cdot IF_5$ and $2\ MoO_3 \cdot 3IF_5$ complexes were formed (74). Reaction of excess IF_5 with $KMnO_4$ gives MnO_3F, IOF_3 [19058-78-7], and IO_2F [28633-62-7] (74).

Water reacts violently with all halogen fluorides. The hydrolysis process can be moderate by cooling or dilution. In addition to HF, the products may include oxygen, free halogens (except for fluorine), and oxyhalogen acids.

Fused silica and Pyrex glass (qv) are not significantly attacked by halogen fluorides up to 100°C if HF is absent.

Salts of halides other than fluorides react with halogen fluorides to produce the corresponding metal fluoride and release the free higher halogen. Filter paper moistened with KI solution darkens readily in the presence of ClF_3 and the bromine fluorides. This serves as a sensitive detector for leaks in equipment containing these halogen fluorides. If a metal exhibits more than one valence, reactions of halogen fluorides with halides (including fluorides) yields the fluoride in which the metal is usually at its highest valence. Chlorine trifluoride converts silver salts to AgF_2, cobalt compounds to CoF_3, and so on. Such reactions are useful in the preparation of fluorinated organic materials and also regenerate fixed-bed fluorinating agents without using fluorine itself (75). A comparison of the efficacy with which various halogen fluorides convert cobalt(II) chloride to cobalt(III) fluoride is indicated below (76).

fluorinating agent	ClF_3	BrF_5	BrF_3	IF_5
solid product	100% CoF_3	55% CoF_3	45% CoF_3	
		45% CoF_2	55% CoF_2	72% CoF_2

3.4. Reactions with Organic Compounds.

Most organic compounds react vigorously exhibiting incandescence or even explosively with ClF_3 and BrF_3 (8,77,78). For this reason, only the less reactive iodine pentafluoride is used as a fluorinating agent to any extent. The reaction of iodine pentafluoride and various organic compounds is described in the literature (79–84).

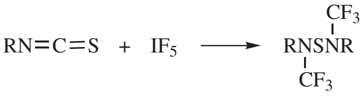
Inert diluents in which the halogen fluorides are soluble, such as carbon tetrachloride and methylene dichloride (85), have been used for control in liquid-phase reactions. Anhydrous hydrogen fluoride is a good diluent, because it does not react with halogen fluorides but rather is miscible in all proportions with them (86). Control of vapor-phase reactions may be improved by diluting the halogen fluoride with an inert gas such as nitrogen or argon. However, any reaction of the halogen fluorides with an organic compound in either the gas or liquid phase should be approached with extreme caution.

Bromine trifluoride in bromine solution reacts smoothly with bromofluoroethanes to give a clean, progressive substitution of the bromine by fluorine with no replacement of the hydrogen (87). The relative ease of replacement of bromine in various groups is $CBr_3 > CBr_2F > CHBr_2 > CF_2Br > CHBrF > CH_2Br$.

The reactions with IF_5 are more amenable to control giving good yields of identifiable products and lower losses from oxidative fragmentation. The reaction of IF_5 and iodine with tetrafluoroethylene produces the telomer perfluoroethyl iodide [354-64-3] in yields that exceed 98% based on $CF_2DBONDCF_2$ using SbF_5 as a catalyst (88).

$$2\,I_2 + IF_5 + 5\,CF_2{=\!=}CF_2 \longrightarrow 5\,CF_3CF_2I$$

Aryl and alkyl isothiocyanates are converted in good yields by IF_5 in pyridine to thiobis(*N*-trifluoromethylamines) (89,90):



$$RN{=}C{=}S + IF_5 \longrightarrow R\underset{CF_3}{N}S\overset{CF_3}{N}R$$

Fluorination of aromatic isothiocyanates occurs much more readily than that of alkyl isothiocyanates. Alcohols treated with IF_5 in DMF give 30–70% yields of their respective formates.

Iodine pentafluoride fluorinates CCl_4 at room temperature to give $CClF_3$ and traces of CCl_2F_2 (91). It reacts with CHI_3 to yield CHF_3 and $CHIF_2$ (92) and with CI_4 to form C_2F_2 (92) and CIF_3 (93). With CBr_4 at 90°C, IF_5 forms 83% CBr_2F_2 and minor amounts of CBr_3F and $CBrF_3$.

Table 2. **Acids and Bases Derived from Halogen Fluorides**

Name	CAS Registry number	Formula	Reference
	Acid		
difluorobromine hexafluoroantimonate	[19379-47-6]	BrF_2SbF_6	73
bis(difluorobromine) hexafluorostannate	[72229-86-8]	$(BrF_2)_2SnF_6$	73
difluorobromine hexafluoroniobate	[72229-87-9]	BrF_2NbF_6	100
difluorobromine hexafluorotantalate	[35967-87-4]	BrF_2TaF_6	100
difluorobromine hexafluorobismuthate	[36608-81-8]	BrF_2BiF_6	100
tetrafluoroiodine hexafluoroantimonate	[41646-48-4]	IF_4SbF_6	101
	Base		
potassium hexafluorobromate	[32312-22-4]	$KBrF_6$	95
silver tetrafluorobromate	[35967-89-6]	$AgBrF_4$	95
barium tetrafluorobromate	[35967-90-9]	$Ba(BrF_4)_2$	95
potassium hexafluoroiodate	[20916-97-6]	KIF_6	94

3.5. Liquid Halogen Fluorides as Reaction Media.

Bromine trifluoride and iodine pentafluoride are highly dimerized and behave as ionizing solvents:

$$(BrF_3) \rightleftharpoons BrF_2^+ + BrF_4^-$$

$$(IF_5)_2 \rightleftharpoons IF_4^+ + IF_6^-$$

Antimony pentafluoride dissolves in each to form BrF_2^+ SbF_6^- and IF_4^+ SbF_6^- which act as acids. Potassium fluoride likewise forms $KBrF_4$ [15705-87-0] and KIF_6 [20916-97-6] which are both stable, white, crystalline solids (3,94,95). These compounds dissociate at 200°C to KF and the corresponding halogen fluoride. Other salts are formed similarly (71,95–99). Some of the acids and bases of these systems are listed in Table 2.

The use of ClF_3 and BrF_3 as ionizing solvents has been studied (102,103). At 100°C and elevated pressures, significant yields of $KClF_4$ [19195-69-8], $CsClF_4$ [15321-04-7], $RbClF_4$ [15321-10-5], $KBrF_6$ [32312-22-4], $RbBrF_6$ [32312-22-4], and $CsBrF_6$ [26222-92-4] were obtained. Chlorine trifluoride showed no reaction with lithium fluoride or sodium fluoride.

4. Manufacture

4.1. Bromine Trifluoride.

Bromine trifluoride is produced commercially by the reaction of fluorine with bromine in a continuous gas-phase process where the ratio of fluorine to bromine is maintained close to 3:1. It is also produced in a liquid-phase batch reaction where fluorine is added to liquid bromine at a temperature below the boiling point of bromine trifluoride.

4.2. Chlorine Trifluoride.

Chlorine trifluoride is produced commercially by the continuous gas-phase reaction of fluorine and chlorine in a nickel reactor at ca 290°C. The ratio of fluorine to chlorine is maintained slightly in excess of 3:1 to promote conversion of the chlorine monofluoride to chlorine trifluoride. Sufficient time in the reactor must be provided to maintain high conversions to chlorine trifluoride. Temperature control is also critical because the equilibrium shift of chlorine trifluoride to chlorine monofluoride and fluorine is significant at elevated temperatures.

4.3. Iodine Pentafluoride.

Iodine pentafluoride is produced by the reaction of iodine and fluorine. Because iodine has a high melting point, the reaction is either performed in a solvent or the reaction is maintained at a temperature where the iodine is liquid. In a continuous process using a solvent (104), ca 1% I_2 is dissolved in IF_5 and passed to a reactor where it is contacted with F_2 gas. The IF_5 is continuously discharged from the reactor where a small portion is taken off as product and the larger portion of the stream is recycled.

In another process (105), fluorine gas reacts under pressure with liquid I_2 held above its melting point (113°C) but below a temperature (150°C) that would result in the formation of significant amounts of IF_7. Fluorine is added continuously until all the iodine has been converted and yields of IF_5 in excess of 95% are reported. The reaction pressure is ca 300 kPa (3 atm) so that the IF_5 produced in the reaction is maintained as a liquid.

5. Shipping, Specifications, and Analytical Methods

Bromine trifluoride is commercially available at a minimum purity of 98% (106). Free Br_2 is maintained at less than 2%. Other minor impurities are HF and BrF_5. Free Br_2 content estimates are based on color, with material containing less than 0.5% Br_2 having a straw color, and ca 2% Br_2 an amber-red color. Fluoride content can be obtained by controlled hydrolysis of a sample and standard analysis for fluorine content. Bromine trifluoride is too high boiling and reactive for gas chromatographic analysis.

It is shipped as a liquid in steel cylinders in quantities of 91 kg or less. The cylinders are fitted with either a valve or plug to facilitate insertion of a dip tube. Bromine trifluoride is classified as an oxidizer and poison by DOT.

Chlorine trifluoride is commercially available at 99% minimum purity (106) and is shipped as a liquid under its own vapor pressure in steel cylinders in quantities of 82 kg per cylinder or less. Chlorine trifluoride is classified as an oxidizer and poison by DOT.

Iodine pentafluoride is commercially available at a minimum purity of 98% (106). Iodine heptafluoride is the principal impurity and maintained at less than 2%. Free I_2 and HF are minor impurities.

Iodine pentafluoride is shipped as a liquid in steel cylinders in various quantities up to 1350 kg cylinders. It is classified as an oxidizer and poison by DOT.

Volatile impurities, eg, F_2, HF, ClF, and Cl_2, in halogen fluoride compounds are most easily determined by gas chromatography (107–109). The use of Ftoroplast adsorbents to determine certain volatile impurities to a detection limit of 0.01% has been described (110–112). Free halogen and halide concentrations can be determined by wet chemical analysis of hydrolyzed halogen fluoride compounds.

5.1. Handling.

The halogen fluorides are highly reactive compounds and must be handled with extreme caution (113–118). The more reactive compounds, such as bromine trifluoride and chlorine trifluoride, are hypergolic oxidizers and react violently and sometimes explosively with many organic and inorganic materials at room temperature. At elevated temperatures, these cause immediate ignition of most organic substances and many metals.

Materials of Construction. Nickel, Monel, copper, mild steel, 304 stainless steel, and aluminum have been found to be suitable metals of construction for handling halogen fluorides (51). Silver solder is acceptable; lead solder is not recommended. Nickel and Monel are more suitable for elevated temperatures. Steel is not dependable above 150°C. Gaskets may be made of soft copper or calcium fluoride-impregnated polytetrafluoroethylene. Packing and gasketing should have smooth surfaces and the surfaces should be free from organic greases and embedded impurities, which may ignite in the presence of halogen fluorides.

Equipment should be carefully and completely degreased and passivated with low concentrations of fluorine or the gaseous halogen fluoride before use. Special care should be taken that valves are completely disassembled and each part carefully cleaned.

5.2. Disposal.

Moderate amounts of chlorine trifluoride or other halogen fluorides may be destroyed by burning with a fuel such as natural gas, hydrogen, or propane. The resulting fumes may be vented to water or caustic scrubbers. Alternatively, they can be diluted with an inert gas and scrubbed in a caustic solution. Further information on disposal of halogen fluorides is available (113–116).

6. Health and Safety Factors

The time-weighted average (TWA) concentrations for 8-h exposure to bromine trifluoride, bromine pentafluoride, chlorine trifluoride, chlorine pentafluoride, and iodine pentafluoride have been established by ACGIH on a fluoride basis to be 2.5 mg/m^3 (119). NIOSH reports (120) the following inhalation toxicity levels for chlorine trifluoride: LC_{50} monkey, 230 ppm/h; LC_{50} mouse, 178 ppm/h; for chlorine pentafluoride: LC_{50} monkey, 173 ppm/h; mouse, 57 ppm/h.

No toxicity data have been reported on the other halogen fluorides, but all should be regarded as highly toxic and extremely irritating to all living tissue.

7. Uses

Chlorine trifluoride is utilized in the processing of nuclear fuels to convert uranium to gaseous uranium hexafluoride. Chlorine trifluoride has also been used as a low temperature etchant for single-crystalline silicon (121,122). Bromine trifluoride has been used in gas phase silicon etching (123).

Bromine trifluoride and chlorine trifluoride are used in oil-well tubing cutters (65–68). Chemical cutter tools are commercially available for use in wells at any depth. The cutter consists of three tubular chambers with the top chamber carrying an explosive charge, the middle chamber containing the halogen fluoride, and the lower chamber containing a catalyst. At the extreme end is the cutter head which guides the halogen fluoride against the pipe to be cut. Arranged around the head is a row of evenly spaced orifices or nozzles. The cable used to lower the cutter into the hole also serves to carry an electric charge to set off the explosive. The force drives the chemical into the head where it jets out of the orifices under enormous pressure to impinge against the inner walls of the tube to be cut. The catalyst raises the temperature of the halogen fluoride to trigger a high speed reaction so that the tube is cut in a fraction of a second. The cut is clean and unflared. Tension on the pipe at the top of the well aids in completing the separation (see PETROLEUM).

Iodine pentafluoride is an easily storable liquid source of fluorine having little of the hazards associated with other fluorine sources. It is used as a selective fluorinating agent for organic compounds. For example, it adds iodine and fluorine to tetrafluoroethylene in a commercial process to produce a useful telomer (124).

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