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BORON HALIDES

1. Introduction

The boron trihalides boron trifluoride [7637-07-2], BF₃, boron trichloride [10294-34-5], BCl₃, and boron tribromide [10294-33-4], BBr₃, are important industrial chemicals having increased usage as Lewis acid catalysts and in chemical vapor deposition (CVD) processes (see ELECTRONIC MATERIALS). Boron halides are widely used in the laboratory as catalysts and reagents in numerous types of organic reactions and as starting material for many organoboron and inorganic boron compounds. An exhaustive review of the literature on boron halides up to 1984 is available (1–5). Of particular interest are review articles on BCl₃ (1), BBr₃ (2), and boron triiodide [13517-10-7], BI₃ (3). An excellent review on diboron tetrahalides and polyhedral boron halides is available (6).

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2. Physical Properties

Boron trihalides, BX_3 , are trigonal planar molecules which are sp^2 hybridized. The X–B–X angles are 120°. Important physical and thermochemical data are presented in Table 1 (7–13). Additional thermodynamic and spectroscopic data may be found in the literature (1–5).

						Refere	nces	
Property	BF_3	BCl_3	BBr_3	BI ₃	BCl_3	BBr_3	BI_3	BF_3
mp, °C bp, °C density ^a , g/mL (liq)	$-128.37 \\ -99.9$	-107 12.5 1.434 $_4^0$ 1.240 ¹¹	$^{-46}_{91.3}_{2.643^{18}_4}$	$-49.9 \\ 210 \\ 3.35$	7 7 8	7 7 9	7 7	14 14
critical temperature, °C	-12.25 ± 0.03	1.349_4 178.8	300		7	7		14
critical pressure, kPa^b vapor pressure, kPa^b $-80^{\circ}C$ $-40^{\circ}C$ $0^{\circ}C$ $40^{\circ}C$ $80^{\circ}C$ at 145 K ^d at 170 K ^d at 220 K ^d	4984 8.43 80.19 1156	3901.0 0.53 8.9 63.5 243 689	с		10 10	9	11	14
at 260 K^d	4842							14
density critical, d_c , g/cm ³ gas at STP, g/L gas limiting, L_N , g/L liquid, for 148.9 to 170.8 K, g/cm ³	ca 0.591 3.07666 3.02662 1.699– 0.00445 (t + 125 0)							16 17 17 18
viscosity, mPa·s	(l + 120.0)	е	е		8	9		
(= cP) ΔH_0^f , kJ/mol, gas ^f ΔH_{vap} , kJ/mol ^f C_p , J(mol·°C), for gas at 25°C ^f		$-403 \\ 23.8 \\ 62.8$	$-206 \\ 34.3 \\ 67.78$	+18	12 12 10	$12 \\ 12 \\ 10$	12	
C_p , J/(mol·°C), for liquid at 25°Cf		121	128		10	10		
$\Delta H_{ m hydrol}$, kJ/mol, liquid at 25°C ^f		-289	-351		10	10		
$\Delta H_{\rm fus}$, J/g at mp ^f ethalpy of fusion, $\Delta H_{144.45}$, kJ/mol ethalpy of vaporiza-	4.2417 18.46	18			10			19 20
tion, $\Delta H_{154.5}$, KJ/ mol ^{f} entropy, $S_{298.15}$, J/(mol \cdot K) ^{f}	254.3							

		_			
Table 1	Physical	Properties	of the	Boron	Trihalides
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						Refere	nces	
Property	BF_3	BCl_3	BBr_3	BI_3	BCl_3	BBr_3	BI_3	BF_3
Gibbs free energy of formation, $\Delta G_f 298.15' \text{ kJ/mol}^f$	-1119.0							
enthalpy of formation, $\Delta H_f 298.15$ ' kJ/mol ^f infrared absorption	-1135.6							21
$frequencies, cm^{-1}$	222							
V ₁	888							
v_2	090.7							
v ₃	1403.3							
B-X bond energy, kJ/ mol ^f	480.7	-443.9	368.2	266.5	13	13	13	
B–X distance, nm	$0.1307 {\pm} 0.002$	0.173	0.187	0.210	13	13	13	21

Table 1 (Cotinued)

^a For BCl₃: $\rho = 1.3730 - 2.159 \times 10^{-3}$ °C - 8.377 × 10^{-7°}C; from -44 to 5°C. Superscript indicates temperature of measurement. For BBr₃: $\rho = 2.698 - 2.996 \times 10^{-3}$ °C; from -20 to 90°C.

^b To convert kPa to mm Hg, multiply by 7.50.

 $\label{eq:ForBBr3:log(pressure)} \ensure{2mm} ^{c} For \ensure{2mm} BBr_3: \ensure{2mm} \log(pressure) = [6.9792 - 1311/(^{\circ}C + 230)] - 0.8752; \ensure{2mm} from \ensure{2mm} 0 - 90^{\circ}C.$

^d Liquid.

^e For BCl₃: $\eta = 0.34417/(1 - 6.9662 \times 10^{-3\circ}\text{C} - 5.9013 \times 10^{-6\circ}\text{C})$; from -40 to 10°C.For BBr₃: log $\eta = (333/\text{K}) - 1.257$; from 0–90°C.

^fTo convert J to cal, divide by 4.184.

Nuclear magnetic resonance ^{11}B spectral studies of BF₃ have given a value of 9.4 \pm 1.0 ppm for the chemical shift relative to BF₃·O(C₂H₅)₂ as the zero reference (22). Using methylcyclohexane as a solvent at 33.5°C and BF₃·O(CH₂CH₃)₂ as the internal standard, a value of 10.0 \pm 0.1 ppm was obtained for the chemical shift (23). A value for the ^{19}F chemical shift of BF₃ in CCl₃F relative to CCl₃F is reported to be 127 ppm (24). The coupling constant J_{11_B}-19_F is reported to be 15 \pm 2 Hz for BF₃ (25). Additional constants are available (26,27). See Table 2 for solubilities.

		Temperature,		CAS Registry	
BF ₃ , g	Solvent, g	$^{\circ}\mathrm{C}$	Product	Number	Reference
369.4	water, ^{<i>a</i>} 100^{b}	6	$\begin{array}{c} BF_3 {\cdot} H_2 O \\ HBF_3 (OH) \end{array}$	[15799-89-0] [16903-52-9]	28
2.06	sulfuric acid, conc, 100% nitric acid ^a orthophosphoric acid ^a	$25 \\ 20 \\ 25$	$HNO_3 \cdot 2BF_3$ $H_3PO_4 \cdot BF_3$	[20660-63-3] [13699-76-6]	29 30 31
2.18	hydrofluoric acid, ^c hydrochloric acid, anhydrous (l)	$\begin{array}{c} 4.4\\24\end{array}$	miscible		$\begin{array}{c} 33\\ 34 \end{array}$

Table 2. Solubilities of Boron Trifluoride

^a Dissolves with reaction to form complexes and other species.

^bA higher dilution results in a mixture of H[BF₂(OH)₂], HBF₄, and H₃BO₃.

^c Equations for the solubility of BF₃ in liquid HF at 24, 49, and 90°C and up to 6.8 kPa (51 mm Hg) may be found in Reference 32.

3. Chemical Properties

The boron trihalides are strong Lewis acids, however, the order of relative acid strengths, $BI_3 \ge BBr_3 > BCl_3 > BF_3$, is contrary to that expected based on the electronegativities and atomic sizes of the halogen atoms. This anomaly has been explained in terms of boron-halogen π -bonding, which increases from BI_3 to BF_3 (35,36). The Lewis acidity of the boron trihalides strongly influences their chemistry (37–40). The trihalides react with Lewis bases containing O, S, N, P, or As atoms to form donor-acceptor complexes. For donor compounds containing active hydrogen, such as NH_3 , PH_3 , AsH_3 , primary and secondary amines, and lower alcohols, BCl_3 , BBr_3 , and BI_3 react to liberate the corresponding hydrogen halide. Tertiary alcohols and the boron trihalides yield the alkyl halide and boric acid. The boron trihalides hydrolyze readily in water or moist air to produce boric acid and hydrogen halides.

 BCl_3 , BBr_3 , and BI_3 undergo exchange reactions to yield mixed boron halides. Exchange reactions also occur with trialkyl, triaryl, trialkoxy, or triaryloxy boranes and with diborane. Anhydrous metal bromides and iodides can be prepared by the exchange reaction of the metal chloride or oxide and BBr_3 or BI_3 (41).

Boron trihalides can be reduced to elemental boron by heating and presence of alkali metals, alkaline-earth metals, or H₂ (42–46); such reductions can also yield boron subhalides, eg, chloroborane [20583-55-5], BCl, B_xCl_x , dichloroborane [10325-29-0], HBCl₂, (47–50), and/or diborane [19287-45-7], B_2H_6 (47–50). Metal hydrides also react with BX₃ to yield diborane (51–53).

Some of the general reactions for the boron trihalides where X represents Cl, Br, or I and X' a different halogen, are

$$B(OH)_{3} + HX \xrightarrow{H_{2}O} R_{3}N = R_{$$

Reactions of boron trihalides that are of commercial importance are those of BCl₃, and to a lesser extent BBr₃, with gases in chemical vapor deposition (CVD). CVD of boron by reduction, of boron nitride using NH₃, and of boron carbide using CH₄ on transition metals and alloys are all technically important processes (54-58). The CVD process is normally supported by heating or by plasma formed by an arc or discharge (59,60).

Aqueous mineral acids react with BF_3 to yield the hydrates of BF_3 or the hydroxyfluoroboric acids, fluoroboric acid, or boric acid. Solution in aqueous alkali gives the soluble salts of the hydroxyfluoroboric acids, fluoroboric acids,

Reactant	$Temperature, ^{\circ}C$	Products	Formula	Reference
sodium ^a		boron, amorphous, sodium fluoride	NaF	61
magnesium, molten alloys	no reaction			
calcium	1600	calcium hexaboride	CaB_6	
aluminum	1200	aluminum boride (1:12), tetragonal boron	AlB_{12}	
	1650^b	β-rhombohedral boron		
titanium	1600	titanium boride	TiB_2	62
copper, mercury, chromium, iron	RT or below	no reaction ^c	_	
sodium nitrate, sodium nitrite	180	sodium fluoroborate, boric oxide	$NaBF_4$	63

Table 3. Reactions of Boron Trifluoride

^a With incandescence.

^b Further reaction.

^c Even when subjected to pressure for a considerable length of time; also no reaction with red-hot iron.

or boric acid. Boron trifluoride, slightly soluble in many organic solvents including saturated hydrocarbons (qv), halogenated hydrocarbons, and aromatic compounds, easily polymerizes unsaturated compounds such as butylenes (qv), styrene (qv), or vinyl esters, as well as easily cleaved cyclic molecules such as tetrahydrofuran. Other molecules containing electron-donating atoms such as O, S, N, P, etc, eg, alcohols, acids, amines, phosphines, and ethers, may dissolve BF₃ to produce soluble adducts.

In addition to the reactions listed in Table 3, boron trifluoride reacts with alkali or alkaline-earth metal oxides, as well as other inorganic alkaline materials, at 450°C to yield the trimer trifluoroboroxine [13703-95-2], (BOF)₃, MBF₄, and MF (64) where M is a univalent metal ion. The trimer is stable below -135° C but disproportionates to B₂O₃ and BF₃ at higher temperatures (65).



The reaction of metal hydrides and BF_3 depends on the stoichiometry as well as the nature of the metal hydride. For example, LiH and $BF_3 \cdot O(C_2H_5)_2$ may form diborane (14) or lithium borohydride (66,67):

$$\begin{split} & 6 \operatorname{LiH} + 8 \operatorname{BF}_3 \cdot \operatorname{O}(\operatorname{C}_2\operatorname{H}_5)_2 \longrightarrow \operatorname{B}_2\operatorname{H}_6 + 6 \operatorname{LiBF}_4 + 8 \operatorname{(C}_2\operatorname{H}_5)_2\operatorname{O} \\ & 4 \operatorname{LiH} + 4 \operatorname{BF}_3 \cdot \operatorname{O}(\operatorname{C}_2\operatorname{H}_5)_2 \longrightarrow \operatorname{LiBH}_4 + 3 \operatorname{LiBF}_4 + 4 \operatorname{(C}_2\operatorname{H}_5)_2\operatorname{O} \end{split}$$

The first method is commonly used for preparing diborane.

Metal halides react with BF_3 (68) when heated to form BX_3 and the metal fluoride. For example,

$$\mathrm{AlBr}_3 + \mathrm{BF}_3 \longrightarrow \mathrm{BBr}_3 + \mathrm{AlF}_3$$

The reaction of BF_3 with alkali halides yields the respective alkali fluoroborates (69):

$$3 \text{ KCl} + 4 \text{ BF}_3 \longrightarrow 3 \text{ KBF}_4 + \text{BCl}_3$$

Alkyl and arylboranes are obtained (70) from BF_3 using the appropriate Grignard reagent, alkylaluminum halide, or zinc alkyl, using diethyl ether as the solvent:

$$BF_3 + 3 RMgX \longrightarrow BR_3 + 3 MgXF$$

Tetraorganylborate complexes may be produced when tetrahydrofuran is the solvent (71).

Alkylfluoroboranes result from the reaction of the appropriate alkylborane and BF_3 under suitable conditions (72):

$$BR_3 + 2(C_2H_5)_2O \cdot BF_3 \longrightarrow 3 \ RBF_2 + 2 \ (C_2H_5)_2O$$

Adducts of BF₃ and some organic compounds having labile hydrogen atoms in the vicinity of the atom bonding to the boron atom of BF₃ may form a derivative of BF₃ by splitting out HF. For example, β -diketones such as acetylacetone or benzoylacetone react with BF₃ in benzene (73):

$$BF_3 + CH_3COCH_2COCH_3 \longrightarrow CH_3COCH = C(CH_3)OBF_2 + HF$$

In Group 14 (IV), carbon serves as a Lewis base in a few of its compounds. In general, saturated aliphatic and aromatic hydrocarbons are stable in the presence of BF₃, whereas unsaturated aliphatic hydrocarbons, such as propylene or acetylene, are polymerized. However, some hydrocarbons and their derivatives have been reported to form adducts with BF₃. Typical examples of adducts with unsaturated hydrocarbons are 1:1 adducts with tetracene and 3,4-benzopyrene (74), and 1:2 BF₃ adducts with α -carotene and lycopene (75).

In Group 15 (V), nitrogen compounds readily form molecular compounds with BF_3 . Phosphorus compounds also form adducts with BF_3 . Inorganic or organic compounds containing oxygen form many adducts with boron trifluoride, whereas sulfur and selenium have been reported to form only a few (76–78).

Boron trifluoride forms two hydrates, $BF_3 \cdot H_2O$ and boron trifluoride dihydrate [13319-75-0], $BF_3 \cdot 2H_2O$, (also $BF_3 \cdot D_2O$ [33598-66-2] and $BF_3 \cdot 2D_2O$ [33598-66-2]). According to reported nmr data (78,79), the dihydrate is ionic, $H_3O^+F_3BOH^-$. The trihydrate has also been reported (80). Acidities of BF_3 -water systems have been determined (81). Equilibrium and hydrolysis of BF_3 in water have been studied (82–84).

Most of the coordination compounds formed by trifluoroborane are with oxygen-containing organic compounds (Table 4). Although the other boron halides frequently react to split out hydrogen halide, boron trifluoride usually forms stable molecular compounds. The reason is attributed to the back coordination of electrons from fluorine to boron forming a strong B-F bond which is 28% ionic (85).

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	A 11	CAS Registry	
Donor	Adduct name	Number	Molecular formula
alcohols	ethanol trifluoroborane	[353-41-3]	$C_2H_5OH \cdot BF_3$
	bis(ethanol)trifluoroborane	[373-59-1]	$2C_2H_5OH \cdot BF_3$
	bis(2-chloroethanol)trifluoroborane	[72985 - 81 - 0]	2 ClCH $_2$ CH $_2$ OH \cdot BF $_3$
	benzyl alcohol trifluoroborane	[456-31-5]	$C_6H_5CH_2OH \cdot BF_3$
acids	acetic acid trifluoroborane	[753-53-7]	$CH_{3}COOH \cdot BF_{3}$
	bis(acetic acid)trifluoroborane	[373-61-5]	$2CH_3COOH \cdot BF_3$
	stearic acid trifluoroborane	[60274 - 92 - 2]	CH ₃ (CH ₂) ₁₆ COOH·BF ₃
	bis(phenol)trifluoroborane	[462-05-5]	$2C_6H_5OH \cdot BF_3$
ethers	diethyl ether trifluoroborane	[109-63-7]	$(C_2H_5)_2O \cdot BF_3$
	tetrahydrofuran trifluoroborane	[462 - 34 - 0]	$(CH_2)_4O \cdot BF_3$
	anisole trifluoroborane	[456-31-5]	$CH_3OC_6H_5 \cdot BF_3$
acid anhydride	acetic anhydride trifluoroborane	[591-00-4]	$(CH_3CO)_2O \cdot BF_3$
esters	ethyl formate trifluoroborane	[462 - 33 - 9]	$HCOOC_2H_5 \cdot BF_3$
	phenyl acetate trifluoroborane	[30884-81-6]	$CH_3COOC_6H_5 \cdot BF_3$
ketones	acetone trifluoroborane	[661-27-8]	$(CH_3)_2CO \cdot BF_3$
	benzophenone trifluoroborane	[322 - 21 - 4]	$(C_6H_5)_2CO \cdot BF_3$
	acetphenone trifluoroborane	[329-25-9]	$C_6H_5COCH_3 \cdot BF_3$
aldehydes	acetaldehyde trifluoroborane	[306-73-0]	$CH_3CHO \cdot BF_3$
	neopentanal trifluoroborane	[306-78-5]	$(CH_3)_3CCHO \cdot BF_3$
	benzaldehyde trifluoroborane	[456-30-4]	$C_6H_5CHO \cdot BF_3$

Table 4. Boron Trifluoride Adducts with Oxygen-Containing Compounds

It has been reported (86) that some adducts of alkyl ethers and/or alcohols are unstable and decompose at -80° C to yield BF₃, H₂O, and the polyalkene. Adducts of BF₃ have been reported with hydrogen sulfide, sulfur dioxide, thionyl fluoride, and the sulfur analogues of many of the kind of oxygen-containing organic molecules cited in Table 4. The carbonyl oxygen or the carbonyl sulfur is the donor to BF₃ in 1:1 adducts such as CH₃COOCH₃·BF₃ [7611-14-5], CH₃COSCH₃·BF₃ [52913-04-9], and CH₃CSOCH₃·BF₃ [52912-98-8] (87).

Compounds containing fluorine and chlorine are also donors to BF_3 . Aqueous fluoroboric acid and the tetrafluoroborates of metals, nonmetals, and organic radicals represent a large class of compounds in which the fluoride ion is coordinating with trifluoroborane. Representative examples of these compounds are given in Table 5. Coordination compounds of boron trifluoride with the chlorides of sodium, aluminum, iron, copper, zinc, tin, and lead have been indicated (88); they are probably chlorotrifluoroborates.

Table 5.	Boron	Trifluoride A	dducts with	Compo	ounds C	Containin	g Chlori	ine and	Fluorine

Name	CAS Registry Number	Molecular formula
potassium tetrafluoroborate hexaamminenickel(II) tetrafluoroborate nitrosyl tetrafluoroborate acetylium tetrafluoroborate tetramethylammonium tetrafluoroborate difluorobromine tetrafluoroborate anilinium tetrafluoroborate	$\begin{matrix} [14075-53-7] \\ [13877-20-8] \\ [14635-75-7] \\ [2261-02-1] \\ [661-36-9] \\ [14282-83-8] \\ [15603-97-1] \end{matrix}$	$\begin{array}{c} KBF_4 \\ [Ni(NH_3)_6](BF_4)_2 \\ NOBF_4 \\ CH_3COBF_4 \\ (CH_3)_4NBF_4 \\ BrF_2BF_4 \\ C_6H_5NH_2HBF_4 \end{array}$

Trifluoroborane may form adducts with some of the transition elements. See Reference 89 for a detailed discussion of complexes of trifluoroborane with various Group 6–10 (VI, VII, and VIII) species.

4. Manufacture

4.1. Boron Trifluoride. Boron trifluoride is prepared by the reaction of a boron-containing material and a fluorine-containing substance in the presence of an acid. The traditional method used borax, fluorspar, and sulfuric acid.

In another process fluorosulfonic acid is treated with boric acid:

 $3 \ HSO_3F + H_3BO_3 \longrightarrow BF_3 + 3 \ H_2SO_4$

Numerous other reactions are available for the preparation of small quantities of boron trifluoride, some of which are of high purity (90,91). A process for recovering boron trifluoride from oligomerization mix have been reported (92).

4.2. Boron Trichloride. Boron trichloride is prepared on a large scale by the reaction of Cl_2 and a heated mixture of borax [1303-96-4], $Na_2BO_4O_7 \cdot 10H_2O$, and crude oil residue (93) in a rotary kiln heated to $1038^{\circ}C$. Borax is fed at the rate of 1360 kg/h and sprayed with 635 kg/h of 17% residue crude oil. The heated mixture then reacts with Cl_2 at 760°C in a separate reactor to yield BCl₃. On a smaller scale, BCl₃ can be prepared by the reaction of Cl_2 and a mixture of boron oxide [1303-86-2], B_2O_3 , petroleum coke, and lampblack in a fluidized bed (94). Other methods for the preparation of BCl₃ from oxygencontaining boron compounds are also known (1,95–98).

A convenient laboratory method for the preparation of BCl₃ is by the reaction of AlCl₃ and BF₃ or BF₄⁻ (99–101). A patent describes the preparation of BCl₃ by halogenating B(OH)₃ or esters of B(OH)₃ using an excess of the oxychloride of S or P in the presence of a dessicant and catalytic amounts of Fe, Co, or Ni, at temperatures below 100°C was issued (102). This process eliminates formation of carbonic dichloride [75-44-5], COCl₂, a common impurity in large-scale production of BCl₃. Other common impurities associated with the preparation of BCl₃ are CO, CO₂, Cl₂, HCl, FeCl₃, SiCl₄, AsCl₃, and SO₂. Methods for purification include distillation (103–105), sometimes in the presence of KCl; activated charcoal or polyphenylene dioxide (106); adsorption desorption on silica gel (107,108); countercurrent crystallization (105); and passage of impure gas through Ti sponge (109), molten Zn (110), Cu or charcoal at elevated temperatures (111). $COCl_2$ can also be destroyed by pyrolysis (112), by a discharge, or irradiation using a radio frequency or an electron beam (113,114), or by uv photolysis using a laser (112,115,116). A system for purification of boron trichloride so that there is less than 10 ppm of phosgene, chlorine, and HCl has been reported (117).

4.3. Boron Tribromide. Boron tribromide is produced on a large scale by the reaction of Br_2 and granulated B_4C at $850-1000^{\circ}C$ (118) or by the reaction of HBr with CaB_6 at high temperatures (119). Reaction of Br_2 and a mixture of B_4C and CaB_6 at 900–1200°C is used to prepare high purity BBr_3 (120). Another method for preparing high purity BBr_3 is the reaction of the two elements, B and Br_2 , at 750°C in N_2 atmosphere, followed by fractional distillation (121).

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Most of the methods for preparing BBr₃ are similar to those for preparation of BCl₃. A convenient laboratory preparation involves reaction of AlBr₃ and BF₃ or BF₄⁻ (2). A procedure for the preparation of labeled ¹⁰BBr₃ from the reaction of ${}^{10}\text{BF}_{-4}^{-}$ and AlBr₃ has also been described (122).

4.4. Boron Triiodide. Boron triiodide is not manufactured on a large scale. Small-scale production of BI_3 from boron and iodine is possible in the temperature range 700–900°C (123–125). Excess I_2 can be removed as SnI_4 by reaction with Sn, followed by distillation (124). The reaction of metal tetrahydroborates and I_2 is convenient for laboratory preparation of BI_3 (126,127). BI_3 can also be synthesized from B_2H_6 and HI in a furnace at 250°C (128), or by the reaction of B with excess AgI or CuI between 450–700°C, under vacuum (129). High purity BI_3 has been prepared by the reaction of I_2 with mixtures of boron carbide and calcium carbide at elevated temperatures.

In addition to distillation (126), BI_3 can be purified by sublimation under reduced pressure (130).

5. Shipment and Handling

Boron trifluoride gas is nonflammable and is shipped in DOT 3A and 3AA steel cylinders at a pressure of approximately 12,410 kPa (1800 psi). Boron trifluoride is classified as a poison gas, both domestically and internationally. Cylinders must have a poison gas diamond and an inhalation hazard warning label. Tube trailers carry both a poison gas placard and an inhalation hazard warning. Cylinders containing 27.2 kg and tube trailers containing 4.5–10 metric tons are available. If boron trifluoride is compressed using oil as a compressor lubricant, it must not be used with oxygen under pressure nor with gauges, valves, or lines that are to be used with oxygen.

In as much as the gas hydrolyzes readily, all equipment should be purged repeatedly using inert dry gas before admitting boron trifluoride. Under anhydrous conditions, carbon steel equipment is satisfactory. Stainless steel and aluminum silicon bronze may also be used. Stainless steel tubing is recommended for both temporary and permanent connections.

In the presence of moisture, boron trifluoride may be handled in polytetrafluoroethylene (PTFE), polyethylene, Pyrex glass (limit to atmospheric pressure), or Hastelloy C containers. At 600°C, stainless steel (304 L) and Hastelloy N are attacked by BF₃; Hastelloy C is more resistant (131). Kel F and PTFE serve as satisfactory gasket and packing materials, whereas rubber, fiber, polymerizable materials, or organic oxygen- and nitrogen-containing compounds must be avoided. Because boron trifluoride is soluble in, and reacts with, many liquids, the gas must not be introduced into any liquid unless a vacuum break or similar safety device is employed.

 BCl_3 is shipped in steel cylinders (0.9-, 45-, 590-, and 817-kg, net); BBr_3 is shipped in glass bottles (0.45- and 2.3-kg, net) and 91-kg (net) monel drums (10). Both BCl_3 and BBr_3 are classed as corrosive liquids, and must be shipped by private carriers.

	BCl ₃ , wt	%	$\mathrm{BBr}_3,\mathrm{wt}~\%$			
Assay	Specification	Typical	Specification	Typical		
$\begin{array}{c} \mathrm{BX}_3\\ \mathrm{Br}_2\\ \mathrm{Cl}_2 \end{array}$	99.9 min 0.01 max	99.95	99.9 min 0.05 max	99.98 0.01		
$\begin{array}{c} \mathrm{COCl}_2 \\ \mathrm{Si} \end{array}$	0.09 max 0.001 max			0.0002^{b}		

Table 6. Specifications for BCl₃ and BBr₃^a

^a Ref. 134.

^b Other impurities in wt % are typically P, 0.002; Fe, 0.003; and Mg, 0.0002.

6. Specifications and Analytical Methods

Commercial boron trifluoride is usually approximately 99.5% pure. The common impurities are air, silicon tetrafluoride, and sulfur dioxide. An excellent procedure for sampling and making a complete analysis of gaseous boron trifluoride has been developed (132).

Analysis for boron, halide, free halogen, and silicon is carried out by standard methods following hydrolysis of BX_3 (10,133). Specifications for BCl_3 and BBr_3 supplied by Kerr-McGee Corp. are given in Table 6.

7. Health and Safety Factors

Boron trifluoride is primarily a pulmonary irritant. The toxicity of the gas to humans has not been reported (135), but laboratory tests on animals gave results ranging from an increased pneumonitis to death. The TLV is 1 ppm (136,137). Inhalation toxicity studies in rats have shown that exposure to BF₃ at 17 mg/m³ resulted in renal toxicity, whereas exposure at 6 mg/m³ did not result in a toxic response (138). Prolonged inhalation produced dental fluorosis (139). High concentrations burn the skin similarly to acids such as HBF₄ and, if the skin is subject to prolonged exposure, the treatment should be the same as for fluoride exposure and hypocalcemia. No chronic effects have been observed in workers exposed to small quantities of the gas at frequent intervals over a period of years.

Boron trichlorides are highly reactive, toxic, and corrosive; these trihalides (BCl_3, BBr_3, BI_3) react vigorously, even explosively, with water. High temperature decomposition of BX_3 can yield toxic halogen-containing fumes. Boron trichloride is a poison by inhalation and a severe irritant to skin, eyes and mucous membranes. BCl_3 , BBr_3 , and BI_3 emit toxic fumes when heated to decomposition (141). Safe handling, especially of BCl_3 , has been reviewed (10,140).

8. Uses

8.1. Boron Trifluoride. Boron trifluoride is an excellent Lewis acid catalyst for numerous types of organic reactions. Its advantages are ease of

handling as a gas and the absence of undesirable tarry by-products. As an electrophilic molecule, it is an excellent catalyst for Friedel-Crafts and many other types of reactions (142–144) (see FRIEDEL-CRAFTS REACTIONS).

BF₃·HF compositions have been reported to act as super acids in catalyzing condensation reactions (145). BF₃-catalyzed preparation of 1- or 2-naphthol is reported to be regioselective (146). Dehydration reactions may also be regioselective (147). Selected fluorinations may be catalyzed by BF₃ using HF as the fluoride source (148). BF₃ is widely used for the preparation of hydrocarbon resins (149), tall oil (qv) resins (150), and tackifier resins (151). Alpha olefin-based synthetic lubricants are commonly made using BF₃-based catalysts (152–154). BF₃ is widely used as a polymerization catalyst (155–157). A developing use for BF₃ is as an ion implant medium for semiconductor materials (158). BF₃ may be used as a chemical reagent for the manufacture of fluoroboro complexes (159), boron nitride [10043-11-5] (160), and boron trichloride [10294-34-5] (161). Carboxylic acids and esters may be prepared by reacting CO with olefins in the presence of BF₃-containing catalysts (152).

In addition, boron trifluoride and some of its adducts have widespread application as curing agents for epoxy resins (qv), and in preparing alcohol-soluble phenolic resins (qv) (76).

Boron trifluoride catalyst is used under a great variety of conditions either alone in the gas phase or in the presence of many types of promoters. Many boron trifluoride coordination compounds are also used.

Boron trifluoride catalyst may be recovered by distillation, chemical reactions, or a combination of these methods. Ammonia or amines are frequently added to the spent catalyst to form stable coordination compounds that can be separated from the reaction products. Subsequent treatment with sulfuric acid releases boron trifluoride. An organic compound may be added that forms an adduct more stable than that formed by the desired product and boron trifluoride. In another procedure, a fluoride is added to the reaction products to precipitate the boron trifluoride which is then released by heating. Selective solvents may also be employed in recovery procedures (see CATALYSTS, REGENERATION).

Boron trifluoride is also employed in nuclear technology by utilizing several nuclear characteristics of the boron atom. Of the two isotopes, ¹⁰B and ¹¹B, only ¹⁰B has a significant absorption cross section for thermal neutrons. It is used in ¹⁰BF₃ as a neutron-absorbing medium in proportional neutron counters and for controlling nuclear reactors (qv). Some of the complexes of trifluoroborane have been used for the separation of the boron isotopes and the enrichment of ¹⁰B as ¹⁰BF₃ (163).

Boron trifluoride is used for the preparation of boranes (see BORON COM-POUNDS). Diborane is obtained from reaction with alkali metal hydrides; organoboranes are obtained with a suitable Grignard reagent.

Boron trifluoride has been used in mixtures to prepare boride surfaces on steel (qv) and other metals, and as a lubricant for casting steel (see LUBRICATION AND LUBRICANTS).

8.2. Boron Trichloride. Much of the BCl_3 consumed in the United States is used to prepare boron filaments by CVD. These high performance fibers are used to reinforce composite materials (qv) made from epoxy resins and metals

(Al, Ti). The principal markets for such composites are aerospace industries and sports equipment manufacturers.

Another important use of BCl_3 is as a Friedel-Crafts catalyst in various polymerization, alkylation, and acylation reactions, and in other organic syntheses (see FRIEDEL-CRAFTS REACTION). Examples include conversion of cyclophosphazenes to polymers (164,165); polymerization of olefins such as ethylene (128,166–171); graft polymerization of vinyl chloride and isobutylene (172); stereospecific polymerization of propylene (173); copolymerization of isobutylene and styrene (174,175), and other unsaturated aromatics with maleic anhydride (176); polymerization of norbornene (177), butadiene (178); preparation of electrically conducting epoxy resins (179), and polymers containing B and N (180); and selective demethylation of methoxy groups ortho to OH groups (181).

BCl₃ is also used for the production of halosilanes, in the preparation of many boron compounds (1,4,5), in the production of optical wave guides (182), and for the prevention of solid polymer formation in liquid SO₃ (10); for the removal of SiO₂ from SiC powders (183), carbochlorination of kaolinitic ores (184), and removal of impurities from molten Mg (182). It is also used as a critical solvent in metal recovery from chlorination processes (185), for the removal of potential catalyst poisons from hydrocarbon oils (186), and in the production of lithium–thionyl chloride batteries (187). Other than production of boron fibers, important CVD processes involving BCl₃ include: production of boron carbide-coated carbon fiber (188,189); doping Si or Ge with B and for doping electric or photoconducting polymers, in the preparation of scratch-resistant silicon-based coatings, and in glass-fiber technology (5); production of boron nitride (5,190–192), and metal borides (5). BCl₃ is also used in reactive ion etching and plasma etching in the production of silicon-integrated circuits and devices, in the dry etching of boron nitride, gallium arsenide, and SnO₂ (5), and Al–Si (193,194).

8.3. Boron Bromide. A large portion of BBr_3 produced in the United States is consumed in the manufacture of proprietory pharmaceuticals (qv). BBr_3 is used in the manufacture of isotopically enriched crystalline boron, as a Friedel-Crafts catalyst in various polymerization, alkylation, and acylation reactions, and in semiconductor doping and etching. Examples of use of BBr_3 as a catalyst include copolymerization of butadiene with olefins (195); polymerization of ethylene and propylene (196), and *N*-vinylcarbazole (197); in hydroboration reactions and in tritium labeling of steroids and aryl rings (5).

 BBr_3 is a very useful reagent for cleaving ethers, esters, lactones, acetals, and glycosidic bonds; it is used to deoxygenate sulfoxides and in the preparation of image-providing materials for photography (5).

8.4. Boron Triiodide. There are no large-scale commercial uses of boron triiodide. It can cleave ethers without affecting aldehyde groups and thus finds use in the synthesis of the antibiotic frustulosin (198,199). BI₃ is used to prepare SnI_4 , SbI_3 , and TiI_4 (200) in 99–100% yield. It is used to clean equipment for handling UF₆ (201) and in the manufacture of lithium batteries (202).

9. Derivatives

9.1. Fluoroboric Acid and the Fluoroborate Ion. Fluoroboric acid [16872-11-0], generally formulated as HBF₄, does not exist as a free, pure

substance. The acid is stable only as a solvated ion pair, such as $H_3O^+BF_4^-$; the commercially available 48% HBF₄ solution approximates $H_3O^+BF_4^- \cdot 4H_2O$. Other names used infrequently are hydrofluoroboric acid, hydroborofluoric acid, and tetrafluoroboric acid. Salts of the acid are named as fluoroborates or occasionally borofluorides. Fluoroboric acid and its salts were investigated as early as 1809 (203,204). The acid and many transition-metal salts are used in the electroplating (qv) and metal finishing industries. Some of the alkali metal fluoroborates are used in fluxes.

Properties. Fluoroboric acid is stable in concentrated solutions, and hydrolyzes slowly in aqueous solution to hydroxyfluoroborates. For the stability of the fluoroborate species, see Reference 205. The equilibrium quotients Q (206,207) in 1 molal NaCl at 25°C show the strong affinity of boron for fluoride:

 $\begin{array}{rcl} \mathrm{B(OH)_3+F^-} &\rightleftharpoons \mathrm{BF(OH)_3^-} & \log Q = -0.36 \pm 0.19 \\ \mathrm{B(OH)_3+2} \ \mathrm{F^-} + \mathrm{H^+} &\rightleftharpoons \mathrm{BF_2(OH)_2^-} + \mathrm{H_2O} & \log Q = 7.06 \pm 0.02 \\ \mathrm{B(OH)_3+3} \ \mathrm{F^-} + 2 \ \mathrm{H^+} &\rightleftharpoons \mathrm{BF_3OH^-} + 2 \ \mathrm{H_2O} & \log Q = 13.689 \pm 0.003 \\ \mathrm{B(OH)_3+4} \ \mathrm{F^-} + 3 \ \mathrm{H^+} &\rightleftharpoons \mathrm{BF_4^-} + 3 \ \mathrm{H_2O} & \log Q = 19.0 \pm 0.1 \end{array}$

The hydrolysis of BF_4^- occurs stepwise to BF_3OH^- , $BF_2(OH)_2^-$, and $BF(OH)_3^-$. By conductivity measurements the reaction of boric acid and HF was found to form $H[BF_3(OH)]$ [15433-40-6] rapidly; subsequently HBF_4 formed much more slowly from HBF_3OH . These studies demonstrate that BF_4^- is quite stable to hydrolysis yet is slow to form from BF_3OH^- and HF:

$$BF_{4}^{-} + H_{2}O \rightleftharpoons BF_{3}OH^{-} + HF$$

Kinetic results (207) and ¹⁹F nmr experiments (208) illustrate clearly that the hydroxyfluoroborates are in rapid equilibrium and easily exchange fluoride.

Table 7 lists some of the physical properties of fluoroboric acid. It is a strong acid in water, equal to most mineral acids in strength and has a pK_{H_2O} of -4.9 as

Table 7. Physical Properties of Fluoroboric Acid

Property	Value	Reference
heat of formation, kJ/mol ^a		
aqueous, 1 molal, at 25°C	-1527	
from boric oxide and HF (aq)	-123.34	204
BF_{4}^{-} , gas	-1765 ± 42	209
entropy of the BF ₄ ⁻ ion, $J/(mol \cdot K)^a$	167	
specific gravity		
48% soln	1.37	
42% soln	1.32	
30% soln	1.20	
surface tension, 48% soln at 25° C, mN/m(= dyn/cm)	65.3	
ir absorptions, ^b cm ⁻¹	ca 1100	210
• ·	ca 530	

^{*a*} To convert J to cal, divide by 4.184.

^b Generally observed as strong absorptions.

compared to -4.3 for nitric acid (211). The fluoroborate ion contains a nearly tetrahedral boron atom with almost equidistant B–F bonds in the solid state. Although lattice effects and hydrogen bonding distort the ion, the average B–F distance is 0.138 nm; the F–B–F angles are nearly the theoretical 109° (212,213). Raman spectra on molten, ie, liquid NaBF₄ agree with the symmetrical tetrahedral structure (214).

The fluoroborate ion has traditionally been referred to as a noncoordinating anion. It has shown little tendency to form a coordinate–covalent bond with transition metals as do nitrates and sulfates. A few exceptional cases have been reported (215) in which a coordinated BF_4^- was detected by infrared or visible spectroscopy.

Hydroxyfluoroborates are products of the reaction of BF₃ with water; BF₃· $2H_2O$ [13319-75-0] is actually $H_3O^+BF_3OH^-$. Salts such as sodium hydroxyfluoroborate [13876-97-6], NaBF₃OH, are made by neutralizing the acid. The BF₃OH⁻ anions are distorted tetrahedra (216). In the HBO₂-HF system, HBO₂·2HF was found to be HBF₂(OH)₂, dihydroxyfluoroboric acid [17068-89-2] (217).

Manufacture, Shipping, and Waste Treatment. Fluoroboric acid (48%) is made commercially by direct reaction of 70% hydrofluoric acid and boric acid, H_3BO_3 . The reaction is exothermic and must be controlled by cooling.

The commercial product is usually a 48–50% solution which contains up to a few percent excess boric acid to eliminate any HF fumes and to avoid HF burns. Reagent-grade solutions are usually 40%. A 61% solution can be made from metaboric acid, HBO₂, and 70% HF, and a lower grade by direct combination of fluorospar, CaF₂, sulfuric acid, and boric acid (218). The product contains a small amount of dissolved calcium sulfate. A silica-containing (0.11% SiO₂) fluoroboric acid is produced from inexpensive fluorosilicic acid (219). Boric acid is added to a 10% H₂SiF₆ solution and then concentrated in several steps to 45% HBF₄. Granular silicon dioxide must be filtered from the product.

Vessels and equipment must withstand the corrosive action of hydrofluoric acid. For a high quality product the preferred materials for handling HBF_4 solutions are polyethylene, polypropylene, or a resistant rubber such as neoprene (see ELASTOMERS, SYNTHETIC). Where metal must be used, ferrous alloys having high nickel and chromium content show good resistance to corrosion. Impregnated carbon (Carbate) or Teflon can be used in heat exchangers. Teflon-lined pumps and auxilliary equipment are also good choices. Working in glass equipment is not recommended for fluoroboric acid or any fluoroborate.

Fluoroboric acid and some fluoroborate solutions are shipped as corrosive material, generally in polyethylene-lined steel pails and drums or in rigid nonreturnable polyethylene containers. Acid spills should be neutralized with lime or soda ash.

Waste treatment of fluoroborate solutions includes a pretreatment with aluminum sulfate to facilitate hydrolysis, and final precipitation of fluoride with lime (220). The aluminum sulfate treatment can be avoided by hydrolyzing the fluoroborates at pH 2 in the presence of calcium chloride; at this pH, hydrolysis is most rapid at elevated temperature (221).

Analysis. Fluoroboric acid solutions and fluoroborates are analyzed gravimetrically using nitron or tetraphenylarsonsium chloride. A fluoroborate ionselective electrode has been developed (222).

	CAS	Mologular				Density. ^a	Solubility			
Compound	Number	weight	Color	Physical form	Mp, $^{\circ}C$	g/cm ³	$\rm H_2O~g/100~mL^b$	Other	References	
${ m LiBF_4} m NaBF_4$	[14283-07-9] [13755-29-8]	93.74 109.79	white white	orthorhombic $<240^{\circ}$ C a = 0.68358, b = 0.62619, c = 0.67916 nm nonpublic $> 240^{\circ}$ C	406 dec	$\begin{array}{c} 2.47 \\ 210^c \end{array}$	very soluble 108 (26°C)	sl alcohol	204,233 215,233,234	
KBF_4	[14075-53-7]	125.92	colorless	rhombic >240 C rhombic $<283^{\circ}$ C a = 0.7032, b = 0.8674, c = 0.5496 nm cubic $>283^{\circ}$ C	530 dec	2.498	0.45 (20°C) 6.27 (100°C)	sl ethanol insol alkali	233-235	
$RbBF_4$	[18909-68-7]	172.27		orthorhombic $<245^{\circ}$ C a = 0.7296, b = 0.9108, c = 0.5636 nm cubic $>245^{\circ}$ C	612 dec	$\begin{array}{c} 2.820\\ 10^c \end{array}$	0.6 (17°C)		233–235	
$CsBF_4$	[18909-69-8]	219.71	white	orthorhombic $<140^{\circ}$ C a = 0.7647, b = 0.9675, c = 0.5885 nm cubic $>140^{\circ}$ C	555 dec	$\begin{array}{c} 3.20\\ 30^c \end{array}$	1.6 (17°C)		233–235	
NH4BF4	[13826-83-0]	104.84	white	orthorhombic $<205^{\circ}$ C a = 0.7278, b = 0.9072, c = 0.5678 nm	487 dec	1.871 ^{<i>d</i>}	$\begin{array}{c} 3.09\ (-1.0^{\circ}\mathrm{C})\\ 5.26\ (-1.5^{\circ}\mathrm{C})\\ 10.85\ (-2.7^{\circ}\mathrm{C})\\ 12.20\ (0^{\circ}\mathrm{C})\\ 25\ (16^{\circ}\mathrm{C})\\ 25.83\ (25^{\circ}\mathrm{C})\\ 44.09\ (50^{\circ}\mathrm{C})\\ 67.50\ (75^{\circ}\mathrm{C})\\ 98.93\ (100^{\circ}\mathrm{C})\\ 113.7\ (108.5^{\circ}\mathrm{C})\end{array}$	HF^{e}	233,235–237	
NaBF ₃ OH	[13876-97-6]			hexagonal a = 0.8084, c = 0.7958 nm		2.46	(20010 0)		212	

Table 8. General Properties of Metal Fluoroborates

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Health and Safety Factors. Fluoroborates are excreted mostly in the urine (223). Sodium fluoroborate is absorbed almost completely into the human bloodstream and over a 14-d experiment all of the NaBF₄ ingested was found in the urine. Although the fluoride ion is covalently bound to boron, the rate of absorption of the physiologically inert BF_4^- from the gastrointestinal tract of rats exceeds that of the physiologically active simple fluorides (224).

Uses. Printed circuit tin-lead plating is the main use of fluoroboric acid (225). However, the Alcoa Alzak process for electropolishing aluminum requires substantial quantities of fluoroboric acid. A 2.5% HBF₄ solution is used to produce a highly reflective surface (226). The high solubility of many metal oxides in HBF₄ is a decided advantage in metal finishing operations (see METAL SURFACE TREATMENTS). Before plating or other surface treatment, many metals are cleaned and pickled in fluoroboric acid solution; eg, continuous strip pickling of hot-rolled low carbon steel is feasible in HBF₄ solutions (227). Nontempered rolled steel requires 80°C for 60 s in HBF₄ 130 g/L, whereas tempered rolled steel requires only 65°C for 60 s in 65 g/L. The spent pickling solution is recovered by electrodialysis.

Fluoroboric acid is used as a stripping solution for the removal of solder and plated metals from less active substrates. A number of fluoroborate plating baths (228) require pH adjustment with fluoroboric acid (see ELECTROPLATING).

A low grade fluoroboric acid (218) is used in the manufacture of cryolite for the electrolytic production of aluminum:

$4 \operatorname{Na_2SO_4} \cdot \operatorname{NaF} + 5 \operatorname{HBF_4} + 2 \operatorname{Al_2O_3} + 9 \operatorname{H_2O} \longrightarrow 4 \operatorname{Na_3AlF_6} + 5 \operatorname{H_3BO_3} + 4 \operatorname{H_2SO_4}$

The boric and sulfuric acids are recycled to a HBF_4 solution by reaction with CaF_2 . As a strong acid, fluoroboric acid is frequently used as an acid catalyst, eg, in synthesizing mixed polyol esters (229). This process provides an inexpensive route to confectioner's hard-butter compositions which are substitutes for cocoa butter in chocolate candies (see CHOCOLATE AND COCOA). Epichlorohydrin is polymerized in the presence of HBF₄ for eventual conversion to polyglycidyl ethers (230) (see CHLOROHYDRINS). A more concentrated solution, 61–71% HBF₄, catalyzes the addition of CO and water to olefins under pressure to form neo acids (231) (see CARBOXYLIC ACIDS). Deprotection of polymers prepared with selyoxyl protected functional initiators by reaction with agreous fluoroboric aid has been reported (232).

9.2. Main Group. *Properties.* A summary of the chemical and physical properties of alkali-metal and ammonium fluoroborates is given in Tables 8 and 9. Chemically these compounds differ from the transition-metal fluoroborates usually separating in anhydrous form. This group is very soluble in water, except for the K, Rb, and Cs salts which are only slightly soluble. Many of the soluble salts crystallize as hydrates.

Lithium fluoroborate crystallizes from aqueous solutions as $LiBF_4 \cdot 3H_2O$ [39963-05-8] and $LiBF_4 \cdot H_2O$ [39963-03-6]. The heat of dehydration of the monohydrate at 91°C is 70.9 kJ/mol (16.95 kcal/mol); the melting point is 117°C (246). Magnesium, calcium, strontium, and barium fluoroborates crystallize as hydrates: $Mg(BF_4)_2 \cdot 6H_2O$ [19585-07-0], $Ca(BF_4)_2 \cdot 2H_2O$ [27860-81-7], $Sr(BF_4)_2 \cdot 4H_2O$ [27902-05-2], and $Ba(BF_4)_2 \cdot 2H_2O$ [72259-09-7], respectively.

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		T		$\log P$	$P_{\rm Pa} = -aT$				
Compound	$\Delta H_{ m diss}$	Lattice energy $-U$, $\Delta H_{\rm fus}$	ΔH_f	Other	a	b^c	<i>T</i> , °C	References
LiBF₄	15.9	699		-1838.4	$\Delta H^d=-89.54$	833	6.40	210 - 320	238-240
NaBF₄	69.83	657.3	13.6	-1843.5	$\Delta H^e=~-134.1$	3650	8.75	400 - 700	234,239-241
KBF_4	121	598	18.0	-1881.5	$\Delta H^{\!f}\!=~-180.5$	6317	8.15	510 - 830	234,239,240,242,243
					$\Delta H_{\rm sub} = 330$				
					$S = 130^{\circ}$ C = 112.1				
$RbBF_4$	112.8	577	19.6		$C_p = 112.1$	5960	9.57	600 - 1000	234,239,242
$CsBF_4$	112.5	556	19.2			5880	9.47	610 - 1040	234,239,242
NaBF ₃ OH	77.0			-1754		4024	9.11	400 - 700	241
$\rm NH_4BF_4$		607^h			$\Delta H_{ m sub} = 47.3$	2469	8.94		244,245

Table 9. Thermodynamic Data^{*a*} for Metal Fluoroborates, kJ/mol^{*b*}

 $a^{a} \Delta H_{\text{diss}} = \text{heat of dissociation}, \Delta H_{\text{fus}} = \text{heat of fusion}, \Delta H_{f} = \text{heat of formation}, \Delta H_{\text{sub}} = \text{sublimation}.$ All thermodynamic data at 25°C, unless otherwise stated. ^b To convert J to cal, divide by 4.184.

^{*c*} To convert log P_{Pa} to log $P_{mm Hg}$, subtract 2.12 from *b*. ^{*d*} LiF(s) + BF₃(g) \rightarrow LiBF₄(s).

^{*e*} NaF(s) + BF₃(g) \rightarrow NaBF₄(s).

 f KF(s) + BF₃(g) \longrightarrow KBF₄(s).

^g Units are in $J/(mol \cdot K)$.

^h At 260°C.

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These hydrated fluoroborates can be dehydrated completely to the anhydrous salts, which show decreasing stabilities: Ba > Sr > Ca > Mg.

The anhydrous magnesium salt is least stable thermally. It forms MgF₂, which has the highest lattice energy. This has been confirmed by differential thermal analysis (dta) of the crystalline hydrates (247). Aluminum fluoroborate [14403-54-4], Al(BF₄)₃ · (H₂O)_n, is soluble in strongly acid solutions and displays a tendency for fluoride exchange with BF₄⁻ to form aluminum fluorides. The aluminyl compound, AlO⁺BF₄⁻, is extremely hygroscopic and is prepared by the reaction of AlOCl, BF₃, and HF (248). Differential thermal analysis experiments show thermal decomposition beginning at 85°C, corresponding to removal of BF₃ and formation of AlOF.

Differential thermal analysis studies of ammonium fluoroborate showed the orthorhombic to cubic transition at $189 \pm 5^{\circ}$ C and BF₃ generation from 389 to 420°C (249). Sodium hydroxide reacts with NH₄BF₄ liberating ammonia and forming NaBF₄. When sodium fluoroborate was studied by infrared spectroscopy, sodium hydroxyfluoroborate, NaBF₃OH, was found to be present (250). Although pure sodium hydroxyfluoroborate is thermally unstable, decomposing to Na₂B₂F₆O [18953-03-2] and H₂O, in a melt of NaBF₄⁻NaF no instability of the small amount of NaBF₃OH present was detected. Fusion of NaBF₄ or KBF₄ with boric oxide generates BF₃ and complex borates such as KFB₄O₆ (251). Most fluoroborates decompose readily to give BF₃ when treated with sulfuric acid or when calcined (see Table 9 for dissociation pressure). Under strongly basic conditions the chemical equilibrium is shifted away from BF₄⁻ to borates and fluorides.

Manufacture. Fluoroborate salts are prepared commercially by several different combinations of boric acid and 70% hydrofluoric acid with oxides, hydroxides, carbonates, bicarbonates, fluorides, and bifluorides. Fluoroborate salts are substantially less corrosive than fluoroboric acid but the possible presence of HF or free fluorides cannot be overlooked. Glass vessels and equipment should not be used.

Sodium Fluoroborate. Sodium fluoroborate is prepared by the reaction of NaOH or Na_2CO_3 with fluoroboric acid (252), or by treatment of disodium hexafluorosilicate with boric acid.

Potassium Fluoroborate. Potassium fluoroborate is produced as a gelatinous precipitate by mixing fluoroboric acid and KOH or K_2CO_3 . Alternatively, fluorosilicic acid is treated with H_3BO_3 in a 2:1 molar ratio to give HBF₃OH, which reacts with HF and KCl to yield 98% of KBF₄ in 98.5% purity (253). Commercial KBF₄ normally contains less than 1% KBF₃OH.

Ammonium and Lithium Fluoroborates. Ammonia reacts with fluoroboric acid to produce ammonium fluoroborate (254). An alternative method is the fusion of ammonium bifluoride and boric acid (255):

 $2 \ NH_4HF_2 + H_3BO_3 \longrightarrow NH_4BF_4 + 3 \ H_2O + NH_3$

The water and ammonia must be removed from the melt. Lithium hydroxide or carbonate react with HBF_4 to form $LiBF_4$.

Magnesium Fluoroborate. Treatment of magnesium metal, magnesium oxide, or magnesium carbonate with HBF_4 gives magnesium fluoroborate [14708-13-5]. The MgF₂ is filtered and the product is sold as a 30% solution.

Uses. Alkali metal and ammonium fluoroborates are used mainly for the high temperature fluxing action required by the metals processing industries (see METAL SURFACE TREATMENTS; WELDING). The tendency toward BF_3 dissociation at elevated temperatures inhibits oxidation in magnesium casting and aluminum alloy heat treatment.

The molten salts quickly dissolve the metal oxides at high temperatures to form a clean metal surface. Other uses are as catalysts and in fire-retardant formulations (see FLAME RETARDANTS).

The addition of potassium fluoroborate to Potassium Fluoroborate. grinding wheel and disk formulations permits lower operating temperatures (256). Cooler action is desirable to reduce the burning of refractory materials such as titanium and stainless steels. Excellent results in grinding wheels are also obtained with NaBF₄ (257). A process for boriding steel surfaces using B_4C and KBF_4 as an activator improves the hardness of the base steel (258). Fluxes for aluminum bronze and silver soldering and brazing contain KBF_4 (259) (see Solders and brazing filler metals). Fire retardance is imparted to acrylonitrile polymers by precipitating KBF_4 within the filaments during coagulation (260). In polyurethanes, KBF_4 and NH_4BF_4 reduce smoke and increase flame resistance (261). Both the potassium and ammonium salts improve insulating efficiency of intumescent coatings (262). The endothermic characteristics of these fillers (qv) (release of BF₃) counteract the exothermic nature of the intumescent agents (nitroaromatic amines) in the coating. The sodium and potassium salts are claimed to have a synergistic effect with polyhalogenated aromatics that improve flame-retardant properties of polyesters (263). Elemental boron is prepared by the Cooper electrolysis of a KBF_4 melt with B_2O_3 and KCl (264). The boron may be up to 99.5% purity and, if KBF_4 containing the ¹⁰B isotope is used, the product is ¹⁰B which is used in the nuclear energy field as a neutron absorber (see NUCLEAR REACTORS).

Sodium Fluoroborate. Sodium fluoroborate can be used in the transfer of boron to aluminum alloys but the efficiency is lower than for KBF₄ (265). Sodium fluoroborate in an etching solution with sulfamic acid and H₂O₂ aids in removing exposed lead in printed circuit manufacture (266). During the annealing of galvanized iron (galvannealing), the surface becomes oxidized. The resulting oxide coating, which causes difficulty in soldering, can be removed by aqueous NaBF₄ or NH₄BF₄ (267). Work at Oak Ridge National Lab (Tennessee) has shown that a NaBF₄, with 8 mol % NaF, salt mixture could be used as the coolant in the molten breeder reactor (268); in this molten salt at nearly 600°C the corrosion rate of Hastelloy N is about 8 μ m/yr. Sodium fluoroborate acts as a catalyst for cross-linking cotton cellulose with formaldehyde (269); transesterification in the preparation of polycarbonates (270); and preparation of cyclic oligoethers from ethylene oxide (271). Sodium and lithium fluoroborates are effective flame retardants for cotton and rayon (272).

Ammonium Fluoroborate. Ammonium fluoroborate blends with antimony oxide give good results in flame-retarding polypropylene (273). The complete thermal vaporization makes ammonium fluoroborate an excellent gaseous flux for inert-atmosphere soldering (274). A soldering flux of zinc chloride and ammonium fluoroborate is used in joining dissimilar metals such as Al and Cu (275). Ammonium fluoroborate acts as a solid lubricant in cutting-oil emulsions for aluminum rolling and forming.

Lithium Fluoroborate. Lithium fluoroborate is used in a number of batteries (qv) as an electrolyte, for example in the lithium–sulfur battery (276).

Miscellaneous. Flame-resistant cross-linked polyethylene can be made with a number of fluoroborates and antimony oxide. This self-extinguishing material may contain the fluoroborates of NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Sr^{2+} , or Ba^{2+} in amounts of 4–20% (277). Magnesium fluoroborate catalyzes the epoxy treatment of cotton fabrics for permanent-press finishes (278) (see TEXTILES).

9.3. Transition-Metal and Other Heavy-Metal Fluoroborates. The physical and chemical properties are less well known for transition metals than for the alkali metal fluoroborates (Table 10). Most transition-metal fluoroborates are strongly hydrated coordination compounds and are difficult to dry without decomposition. Decomposition frequently occurs during the concentration of solutions for crystallization. The stability of the metal fluorides accentuates this problem. Loss of HF because of hydrolysis makes the reaction proceed even more rapidly. Even with low temperature vacuum drying to partially solve the decomposition, the dry salt readily absorbs water. The crystalline solids are generally soluble in water, alcohols, and ketones but only poorly soluble in hydrocarbons and halocarbons.

Differential thermal analysis in air on the crystalline hexahydrates of Zn, Cd, Fe, Co, and Ni fluoroborates show the loss of BF₃ and H₂O simultaneously at

Compound	CAS Registry Number	Color	Specific gravity	Solubility	Miscellaneous
$ \begin{array}{c} \hline Mn(BF_{4})_{2} \cdot 6H_{2}O \\ Fe(BF_{4})_{2} \cdot 6H_{2}O \\ Co(BF_{4})_{2} \cdot 6H_{2}O \\ Ni(BF_{4})_{2} \cdot 6H_{2}O \\ Cu(BF_{4})_{2} \cdot 6H_{2}O \\ Cu(BF_{4})_{2} \cdot 6H_{2}O \\ AgBF_{4} \cdot H_{2}O \end{array} $	$\begin{matrix} [26044-57-5] \\ [13877-16-2] \\ [15684-35-2] \\ [14708-14-6] \\ [72259-10-0] \\ [72259-11-1] \end{matrix}$	pale pink pale green green blue colorless	$1.982 \\ 2.038 \\ 2.081 \\ 2.136 \\ 2.175$	water, ethanol water, ethanol water, alcohol water, alcohol water, alcohol water, less sol in alcohol, sol benzene, sol ether	dec 200°C, light sensitive
$Zn(BF_4)_2\cdot 6H_2O$	[27860-83-9]	white	2.120	water, alcohol	dehydrates at 60°C
$\begin{array}{l} Cd(BF_4)_2\cdot 6H_2O\\ In(BF_4)_3\cdot xH_2O\\ TlBF_4\cdot H_2O \end{array}$	[27860-84-0] [27765-48-6] [72259-12-2]	white colorless colorless	2.292	water, alcohol water water	orthorhombic, a = 0.947, b = 0.581, c = 0.740 nm, light sensitive
$\operatorname{Sn}(\mathrm{BF}_4)_2 \cdot x\mathrm{H}_2\mathrm{O}$ $\operatorname{Pb}(\mathrm{BF}_4)_2 \cdot \mathrm{H}_2\mathrm{O}$	[72259-13-3] [26916-34-7]	white		water	$\begin{array}{c} Sn(BF_4)_2 \cdot \\ SnF_2 \cdot 5H_2O \\ crystallizes \\ from \ soln \end{array}$

Table 10. Properties of Metal Fluoroborates^a

^{*a*} Crystalline solids (204,279).

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195, 215, 180, 185, and 205°C, respectively (247,280). The dta curves also indicate initial melting at 107, 117, and 150°C for Zn, Cd, and Fe fluoroborates, respectively. The anhydrous metal fluoride and/or oxide is usually isolated. The copper salt also decomposes with liberation of BF₃ and H₂O (281).

The water of hydration of these complexes can be replaced with other coordinating solvents. For example, the ethanol and methanol solvates were made by dissolving the hydrates in triethyl and trimethyl orthoformate, respectively (282,283). The acetic acid solvates are made by treating the hydrates with acetic anhydride (284). Conductivity and visible spectra, where applicable, of the Co, Ni, Zn, and Cu fluoroborates in N,N-dimethylacetamide (L) showed that all metal ions were present as the ML_6^{2+} cations (285). Solvated fluoroborate complexes of Cr^{3+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Cu^+ , and Zn^{2+} in diethyl ether, nitromethane, and benzene solutions have been prepared. Solutions of Ti(BF₄)₃, V(BF₄)₃, and Fe(BF₄)₃ could not be prepared probably because of formation of BF₃ and the metal fluoride (286). Ammonia easily replaces the coordinated water; the products are usually tetrammine or hexammine complexes (204) (see COORDINATION COMPOUNDS). The hexahydrate of Ni(BF₄)₂ was found to be stable from 25 to 100°C; solubility also was determined to 95°C (287). At 120°C the solid decomposed slowly to NiF₂ with loss of HF, H₃BO₃, and H₂O.

Manufacture. The transition- and heavy-metal fluoroborates can be made from the metal, metal oxide, hydroxide, or carbonate with fluoroboric acid. Because of the difficulty in isolating pure crystalline solids, these fluoroborates are usually available as 40-50% solutions, $M(BF_4)_x$. Most of the solutions contain about 1-2% excess fluoroboric acid to prevent precipitation of basic metal complexes. The solutions are usually sold in 19 and 57 L polyethylene containers.

In some cases, particularly with inactive metals, electrolytic cells are the primary method of manufacture of the fluoroborate solution. The manufacture of Sn, Pb, Cu, and Ni fluoroborates by electrolytic dissolution (288,289) is patented. A typical cell for continous production consists of a polyethylenelined tank with tin anodes at the bottom and a mercury pool (in a porous basket) cathode near the top (289). Fluoroboric acid is added to the cell and electrolysis is begun. As tin fluoroborate is generated, differences in specific gravity cause the product to layer at the bottom of the cell. When the desired concentration is reached in this layer, the heavy solution is drawn from the bottom and fresh HBF₄ is added to the top of the cell continuously. The direct reaction of tin with HBF₄ is slow but can be accelerated by passing air or oxygen through the solution (290). The stannic fluoroborate is reduced by reaction with mossy tin under an inert atmosphere. In earlier procedures, HBF₄ reacted with hydrated stannous oxide.

Anhydrous silver fluoroborate [1404-20-2] is made by the addition of BF₃ gas to a suspension of AgF in ethylbenzene (291). An AgBF₄·C₈H₁₀ complex is precipitated with pentane and the complex is washed with pentane to give anhydrous AgBF₄.

Uses. Metal fluoroborate solutions are used primarily as plating solutions and as catalysts. The Sn, Cu, Zn, Ni, Pb, and Ag fluoroborates cure a wide range of epoxy resins at elevated or ambient room temperature (292,293). In the textile industry zinc fluoroborate is used extensively as the curing agent in applying

resins for crease-resistant finishes (294). Emulsions of epoxy resins (295), polyoxymethylene compounds (296), or aziridinyl compounds (297) with $\text{Zn}(\text{BF}_4)_2$ and other additives are applied to the cloth. After the excess is removed, the cloth is dried and later cured at a higher temperature. Similarly treated acrylic textiles using epoxy resins take on an antistatic finish (298), or the acrylic textiles can be coated with 20% $\text{Zn}(\text{BF}_4)_2$ which results in up to 5.5% added solids for a fire-resistant finish (299).

The use of silver fluoroborate as a catalyst or reagent often depends on the precipitation of a silver halide. Thus the silver ion abstracts a Cl⁻ from a rhodium chloride complex, $((C_6H_5)_3As)_2(CO)RhCl$, yielding the cationic rhodium fluoroborate [30935-54-7] hydrogenation catalyst (300). The complexing tendency of olefins for AgBF₄ has led to the development of chemisorption methods for ethylene separation (301,302). Copper(I) fluoroborate [14708-11-3] also forms complexes with olefins; hydrocarbon separations are effected by similar means (303).

The manufacture of linear polyester is catalyzed by Cd, Sn (304), Pb, Zn, or Mn (305) fluoroborates. The Beckmann rearrangement of cyclohexanone oxime to caprolactam is catalyzed by $Ba(BF_4)_2$ [13862-62-9] or $Zn(BF_4)_2$ [13826-88-5] (306). The caprolactam is polymerized to polyamide fibers using $Mn(BF_4)_2$ [30744-82-2] catalyst (307). Nickel and cobalt fluoroborates appear to be good catalysts for the polymerization of conjugated dienes to *cis*-1,4-polydienes; the cis configuration is formed in up to 96% yields (308–310).

Metal fluoroborate electroplating (qv) baths (228,311,312) are employed where speed and quality of deposition are important. High current densities can be used for fast deposition and near 100% anode and cathode efficiencies can be expected. Because the salts are very soluble, highly concentrated solutions can be used without any crystallization. The high conductivity of these solutions reduces the power costs. The metal content of the bath is also easily maintained and the pH is adjusted with HBF₄ or aqueous ammonia. The disadvantages of using fluoroborate baths are treeing, lack of throwing power, and high initial cost. Treeing and throwing power can be controlled by additives; grain size of the deposits can also be changed. As of this writing, metals being plated from fluoroborate baths are Cd, Co, Cu, Fe, In, Ni, Pb, Sb, and Zn. Studies on Fe (313,314), Ni (314), and Co (314) fluoroborate baths describe the compositions and conditions of operation as well as the properties of the coatings. Iron foils electrodeposited from fluoroborate baths and properly annealed have exceptionally high tensile strength (314).

The Fe, Co, and Ni deposits are extremely fine grained at high current density and pH. Electroless nickel, cobalt, and nickel-cobalt alloy plating from fluoroborate-containing baths yields a deposit of superior corrosion resistance, low stress, and excellent hardenability (315). Lead is plated alone or in combination with tin, indium, and antimony (316). Sound insulators are made as lead-plastic laminates by electrolytically coating Pb from a fluoroborate bath to 0.5 mm on a copper-coated nylon or polypropylene film (317) (see INSULATION, ACOUSTIC). Steel plates can be simultaneously electrocoated with lead and poly(tetrafluoroethylene) (318). Solder is plated in solutions containing Pb(BF₄)₂ and Sn(BF₄)₂; thus the lustrous solder-plated object is coated with a Pb-Sn alloy (319).

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