Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINE COMPOUNDS, INORGANIC, FLUOROBORIC ACID AND FLUOROBORATES

1. Fluoroboric Acid and the Fluoroborate Ion

Fluoroboric acid [16872-11-0], generally formulated as HBF_4, 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% HBF_4 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 (1, 2). 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.

1.1. 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 3. The equilibrium quotients Q (4, 5) in 1 molal NaCl at 25°C show the strong affinity of boron for fluoride:

$$B(OH)_3 + F^- \rightleftharpoons BF(OH)_3^- \qquad \log Q = -0.36 \pm 0.19$$

$$B(OH)_3 + 2\,F^- + H^+ \rightleftharpoons BF_2(OH)_2^- + H_2O \qquad \log Q = 7.06 \pm 0.02$$

$$B(OH)_3 + 3\,F^- + 2\,H^+ \rightleftharpoons BF_3OH^- + 2\,H_2O \qquad \log Q = 13.689 \pm 0.003$$

$$B(OH)_3 + 4\,F^- + 3\,H^+ \rightleftharpoons BF_4^- + 3\,H_2O \qquad \log Q = 19.0 \pm 0.1$$

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

Table 1. 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	2
BF_4^-, gas	−1765 ± 42	7
entropy of the BF_4^- ion, J/(mol·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 ca 530	8

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

[b] Generally observed as strong absorptions.

is slow to form from BF_3OH^- and HF:

$$BF_4^- + H_2O \rightleftharpoons BF_3OH^- + HF$$

Kinetic results (5) and ^{19}F nmr experiments (6) illustrate clearly that the hydroxyfluoroborates are in rapid equilibrium and easily exchange fluoride.

Table 1 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 compared to -4.3 for nitric acid (9). 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° (10, 11). Raman spectra on molten, ie, liquid $NaBF_4$ agree with the symmetrical tetrahedral structure (12).

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 (13) in which a coordinated BF_4^- was detected by infrared or visible spectroscopy.

Hydroxyfluoroborates are products of the reaction of BF_3 with water; $BF_3{\cdot}2H_2O$ [13319-75-0] is actually $H_3O^+BF_3OH^-$. Salts such as sodium hydroxyfluoroborate [13876-97-6], $NaBF_3OH$, are made by neutralizing the acid. The BF_3OH^- anions are distorted tetrahedra (14). In the HBO_2–HF system, $HBO_2{\cdot}2HF$ was found to be $HBF_2(OH)_2$, dihydroxyfluoroboric acid [17068-89-2] (15).

1.2. Manufacture, Shipping, and Waste Treatment

Fluoroboric acid (48%) is made commercially by direct reaction of 70% hydrofluoric acid and boric acid, H_3BO_3 (see Boron compounds). 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, HBO_2, and 70% HF, and a lower grade by direct combination of fluorospar, CaF_2, sulfuric acid, and boric acid (16). The product contains a small amount of dissolved calcium sulfate. A silica-containing (0.11% SiO_2) fluoroboric acid is produced from inexpensive fluorosilicic acid (17). Boric acid is added to a 10% H_2SiF_6 solution and then concentrated in several steps to 45% HBF_4. 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 (18). 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 (19).

1.3. Economic Aspects

In the United States fluoroboric acid is manufactured by Atotech USA, Inc., General Chemical, C.P. Chemical Co., Fidelity Chemical Products, and Chemtech Harstan. Research quantities of reagent grade are made by Advance Research Chemical Co., Johnson-Mathey, and Ozark-Mahoning Co. The price for 48% fluoroboric acid in truckload quantities in 1993 was $2.13–2.25/kg (20).

Many specialty fluoroborates are available in research quantities from Advance Research Chemicals.

1.4. Analysis

Fluoroboric acid solutions and fluoroborates are analyzed gravimetrically using nitron or tetraphenylarsonsium chloride. A fluoroborate ion-selective electrode has been developed (21).

1.5. Toxicity

Fluoroborates are excreted mostly in the urine (22). Sodium fluoroborate is absorbed almost completely into the human bloodstream and over a 14-d experiment all of the $NaBF_4$ 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 (23).

1.6. Uses

Printed circuit tin–lead plating is the main use of fluoroboric acid (24). However, the Alcoa Alzak process for electropolishing aluminum requires substantial quantities of fluoroboric acid. A 2.5% HBF_4 solution is used to produce a highly reflective surface (25). The high solubility of many metal oxides in HBF_4 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 HBF_4 solutions (26). Nontempered rolled steel requires 80°C for 60 s in HBF_4 130 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 (27) require pH adjustment with fluoroboric acid (see Electroplating).

A low grade fluoroboric acid (16) is used in the manufacture of cryolite (28) for the electrolytic production of aluminum:

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

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 (29). 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 HBF_4 for eventual conversion to polyglycidyl ethers (30) (see Chlorohydrins). A more concentrated solution, 61–71% HBF_4, catalyzes the addition of CO and water to olefins under pressure to form neo acids (31) (see Carboxylic acids).

2. Main Group

2.1. Properties

A summary of the chemical and physical properties of alkali-metal and ammonium fluoroborates is given in Tables 2 and 3. 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 (45). 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. 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 MgF_2, which has the highest lattice energy. This has been confirmed by differential thermal analysis (dta) of the crystalline hydrates (46). Aluminum fluoroborate [14403-54-4], $Al(BF_4)_3{\cdot}(H_2O)_n$, is soluble in strongly acid solutions and displays a tendency for fluoride exchange with BF_4^- to form aluminum fluorides. The aluminyl compound, $AlO^+BF_4^-$, is extremely hygroscopic and is prepared by the reaction of AlOCl, BF_3, and HF (47). Differential thermal analysis experiments show thermal decomposition beginning at 85°C, corresponding to removal of BF_3 and formation of AlOF.

Differential thermal analysis studies of ammonium fluoroborate showed the orthorhombic to cubic transition at $189 \pm 5°C$ and BF_3 generation from 389 to 420°C (48). Sodium hydroxide reacts with NH_4BF_4 liberating ammonia and forming $NaBF_4$. When sodium fluoroborate was studied by infrared spectroscopy, sodium hydroxyfluoroborate, $NaBF_3OH$, was found to be present (49). Although pure sodium hydroxyfluoroborate is thermally unstable, decomposing to $Na_2B_2F_6O$ [18953-03-2] and H_2O, in a melt of $NaBF_4^-NaF$ no instability of the small amount of $NaBF_3OH$ present was detected. Fusion of $NaBF_4$ or KBF_4 with boric oxide generates BF_3 and complex borates such as KFB_4O_6 (50). Most fluoroborates decompose readily to give BF_3 when treated with sulfuric acid or when calcined (see Table 3 for dissociation pressure). Under strongly basic conditions the chemical equilibrium is shifted away from BF_4^- to borates and fluorides.

2.2. 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

Table 2. General Properties of Metal Fluoroborates

							Solubility		
Compound	CAS Registry Number	Molecular weight	Color	Physical form	Mp, °C	Density,[a] g/cm^3	H_2O g/100 mL[b]	Other	References
$LiBF_4$	[14283-07-9]	93.74	white				very soluble		(2, 32)
$NaBF_4$	[13755-29-8]	109.79	white	orthorhombic $<240°C$ $a = 0.68358$, $b = 0.62619$, $c = 0.67916$ nm noncubic $>240°C$	406 dec	2.47 210[c]	108 (26°C)	sl alcohol	(13, 32, 33)
KBF_4	[14075-53-7]	125.92	colorless	rhombic $<283°C$ $a = 0.7032$, $b = 0.8674$, $c = 0.5496$ nm cubic $>283°C$	530 dec	2.498	0.45 (20°C) 6.27 (100°C)	sl ethanol insol alkali	(32–34)
$RbBF_4$	[18909-68-7]	172.27		orthorhombic $<245°C$ $a = 0.7296$, $b = 0.9108$, $c = 0.5636$ nm cubic $>245°C$	612 dec	2.820 10[c]	0.6 (17°C)		(32–34)
$CsBF_4$	[18909-69-8]	219.71	white	orthorhombic $<140°C$ $a = 0.7647$, $b = 0.9675$, $c = 0.5885$ nm cubic $>140°C$	555 dec	3.20 30[c]	1.6 (17°C)		(32–34)
NH_4BF_4	[13826-83-0]	104.84	white	orthorhombic $<205°C$ $a = 0.7278$, $b = 0.9072$, $c = 0.5678$ nm	487 dec	1.871[d]	3.09 (−1.0°C) 5.26 (−1.5°C) 10.85 (−2.7°C) 12.20 (0°C) 25 (16°C) 25.83 (25°C) 44.09 (50°C) 67.50 (75°C) 98.93 (100°C) 113.7 (108.5°C)	HF[e]	(32, 34, 35) 36
$NaBF_3OH$	[13876-97-6]			hexagonal $a = 0.8084$, $c = 0.7958$ nm		2.46			10

[a] Unless otherwise stated, at 20°C.
[b] Temperature given in parentheses.
[c] At 100°C.
[d] At 15°C.
[e] Value at 0°C is 19.89%.

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.

2.2.1. Sodium Fluoroborate

Sodium fluoroborate is prepared by the reaction of NaOH or Na_2CO_3 with fluoroboric acid (51), or by treatment of disodium hexafluorosilicate with boric acid.

Table 3. Thermodynamic Data[a] for Metal Fluoroborates, kJ/mol[b]

						$\log P_{\mathrm{Pa}} = -aT^{-1} + b$			
Compound	ΔH_{diss}	Lattice energy, $-U$	ΔH_{fus}	ΔH_{f}	Other	a	b^c	T, °C	References
$LiBF_4$	15.9	699		−1838.4	$\Delta H^d = -89.54$	833	6.40	210–320	(37–39)
$NaBF_4$	69.83	657.3	13.6	−1843.5	$\Delta H^e = -134.1$	3650	8.75	400–700	(33, 38–40)
KBF_4	121	598	18.0	−1881.5	$\Delta H^f = -180.5$ $\Delta H_{\mathrm{sub}} = 330$ $S = 130^g$ $C_p = 112.1^g$	6317	8.15	510–830	(33, 38, 39, 41, 42)
$RbBF_4$	112.8	577	19.6			5960	9.57	600–1000	(33, 38, 41)
$CsBF_4$	112.5	556	19.2			5880	9.47	610–1040	(33, 38, 41)
$NaBF_3OH$	77.0			−1754		4024	9.11	400–700	40
NH_4BF_4		607^h			$\Delta H_{\mathrm{sub}} = 47.3$	2469	8.94		(43, 44)

[a] ΔH_{diss} = heat of dissociation, ΔH_{fus} = heat of fusion, ΔH_f = heat of formation, ΔH_{sub} = sublimation. All thermodynamic data at 25°C, unless otherwise stated.

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

[c] To convert $\log P_{\mathrm{Pa}}$ to $\log P_{\mathrm{mmHg}}$, subtract 2.12 from b.

[d] $LiF(s) + BF_3(g) \longrightarrow LiBF_4(s)$.

[e] $NaF(s) + BF_3(g) \longrightarrow NaBF_4(s)$.

[f] $KF(s) + BF_3(g) \longrightarrow KBF_4(s)$.

[g] Units are in J/(mol·K).

[h] At 260°C.

2.2.2. 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 HBF_3OH, which reacts with HF and KCl to yield 98% of KBF_4 in 98.5% purity (52). Commercial KBF_4 normally contains less than 1% KBF_3OH.

2.2.3. Ammonium and Lithium Fluoroborates

Ammonia reacts with fluoroboric acid to produce ammonium fluoroborate (53). An alternative method is the fusion of ammonium bifluoride and boric acid (54):

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

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

2.2.4. Magnesium Fluoroborate

Treatment of magnesium metal, magnesium oxide, or magnesium carbonate with HBF_4 gives magnesium fluoroborate [14708-13-5]. The MgF_2 is filtered and the product is sold as a 30% solution.

2.3. Economic Aspects

In the United States the sodium, potassium, ammonium, and magnesium fluoroborates are sold by Advance Research Chemicals, Atotech USA, Inc., and General Chemical. The lithium compound is available from Advance Research Chemicals, Cyprus Foote Mineral, and FMC Lithium Corp. of America. Small amounts of other fluoroborates are sold by Alfa Inorganics, Inc. and Ozark-Mahoning Co. Prices in 1993 for truckload quantities were $NaBF_4$, \$4.95–6.25/kg; KBF_4, \$3.55/kg; and NH_4BF_4 \$5.03–6.35/kg.

2.4. 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).

2.5. Potassium Fluoroborate

The addition of potassium fluoroborate to grinding wheel and disk formulations permits lower operating temperatures (55). 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 $NaBF_4$ (56). A process for boriding steel surfaces using B_4C and KBF_4 as an activator improves the hardness of the base steel (57). Fluxes for aluminum bronze and silver soldering and brazing contain KBF_4 (58) (see Solders and brazing filler metals). Fire retardance is imparted to acrylonitrile polymers by precipitating KBF_4 within the filaments during coagulation (59). In polyurethanes, KBF_4 and NH_4BF_4 reduce smoke and increase flame resistance (60). Both the potassium and ammonium salts improve insulating efficiency of intumescent coatings (61). The endothermic characteristics of these fillers (qv) (release of BF_3) 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 (62). Elemental boron is prepared by the Cooper electrolysis of a KBF_4 melt with B_2O_3 and KCl (63). The boron may be up to 99.5% purity and, if KBF_4 containing the ^{10}B isotope is used, the product is ^{10}B which is used in the nuclear energy field as a neutron absorber (see Nuclear reactors).

2.5.1. Sodium Fluoroborate

Sodium fluoroborate can be used in the transfer of boron to aluminum alloys but the efficiency is lower than for KBF_4 (64). Sodium fluoroborate in an etching solution with sulfamic acid and H_2O_2 aids in removing exposed lead in printed circuit manufacture (65). 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 $NaBF_4$ or NH_4BF_4 (66). Work at Oak Ridge National Lab (Tennessee) has shown that a $NaBF_4$, with 8 mol % NaF, salt mixture could be used as the coolant in the molten breeder reactor (67); in this molten salt at nearly 600°C the corrosion rate of Hastelloy N is about 8 μm/yr. Sodium fluoroborate acts as a catalyst for cross-linking cotton cellulose with formaldehyde (68); transesterification in the preparation of polycarbonates (69); and preparation of cyclic oligoethers from ethylene oxide (70). Sodium and lithium fluoroborates are effective flame retardants for cotton and rayon (71).

2.5.2. Ammonium Fluoroborate

Ammonium fluoroborate blends with antimony oxide give good results in flame-retarding polypropylene (72). The complete thermal vaporization makes ammonium fluoroborate an excellent gaseous flux for inert-atmosphere soldering (73). A soldering flux of zinc chloride and ammonium fluoroborate is used in joining dissimilar metals such as Al and Cu (74). Ammonium fluoroborate acts as a solid lubricant in cutting-oil emulsions for aluminum rolling and forming.

Table 4. Properties of Metal Fluoroborates[a]

Compound	CAS Registry Number	Color	Specific gravity	Solubility	Miscellaneous
$Mn(BF_4)_2{\cdot}6H_2O$	[26044-57-5]	pale pink	1.982	water, ethanol	
$Fe(BF_4)_2{\cdot}6H_2O$	[13877-16-2]	pale green	2.038	water, ethanol	
$Co(BF_4)_2{\cdot}6H_2O$	[15684-35-2]	red	2.081	water, alcohol	
$Ni(BF_4)_2{\cdot}6H_2O$	[14708-14-6]	green	2.136	water, alcohol	
$Cu(BF_4)_2{\cdot}6H_2O$	[72259-10-0]	blue	2.175	water, alcohol	
$AgBF_4{\cdot}H_2O$	[72259-11-1]	colorless		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
$Cd(BF_4)_2{\cdot}6H_2O$	[27860-84-0]	white	2.292	water, alcohol	
$In(BF_4)_3{\cdot}xH_2O$	[27765-48-6]	colorless		water	
$TlBF_4{\cdot}H_2O$	[72259-12-2]	colorless		water	orthorhombic, $a = 0.947$, $b = 0.581$, $c = 0.740$ nm, light sensitive
$Sn(BF_4)_2{\cdot}xH_2O$	[72259-13-3]	white		water	$Sn(BF_4)_2{\cdot}SnF_2{\cdot}5H_2O$ crystallizes from soln
$Pb(BF_4)_2{\cdot}H_2O$	[26916-34-7]	colorless			

[a] Crystalline solids (2, 78).

2.5.3. Lithium Fluoroborate

Lithium fluoroborate is used in a number of batteries (qv) as an electrolyte, for example in the lithium–sulfur battery (75).

2.5.4. 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% (76). Magnesium fluoroborate catalyzes the epoxy treatment of cotton fabrics for permanent-press finishes (77) (see Textiles).

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 4). 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 BF_3 and H_2O simultaneously at 195, 215, 180, 185, and 205°C, respectively (46, 79). 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 BF_3 and H_2O (80).

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 (81, 82). The acetic acid solvates are made by treating the hydrates with acetic

Table 5. Commercial Metal Fluoroborate Solutions

Metal cation	CAS Registry Number	Formula	% Metal	Specific gravity, g/cm^3	1992 price, \$/kg
antimony(II)	[14486-20-5]	$Sb(BF_4)_3$	12.8	1.42	
cadmium	[14886-19-2]	$Cd(BF_4)_2$	19.7	1.60	8.15
cobalt(II)	[26490-63-1]	$Co(BF_4)_2$	11.8	1.42	
copper(II)	[38465-60-0]	$Cu(BF_4)_2$	12.2	1.48	3.40–4.0
indium	[27765-48-6]	$In(BF_4)_3$	15.3	1.55	
iron(II)	[13877-16-2]	$Fe(BF_4)_2$	10.3	1.47	
lead(II)	[13814-96-5]	$Pb(BF_4)_2$	28.9	1.75	1.85–2.16
nickel(II)	[14708-14-6]	$Ni(BF_4)_2$	11.2	1.47	10.25–11.8
tin(II)	[13814-96-5]	$Sn(BF_4)_2$	20.2	1.61	6.38–6.6
zinc	[13826-88-5]	$Zn(BF_4)_2$	11.0	1.39	1.75–2.1

anhydride (83). 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 (84). 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 $Ti(BF_4)_3$, $V(BF_4)_3$, and $Fe(BF_4)_3$ could not be prepared probably because of formation of BF_3 and the metal fluoride (85). Ammonia easily replaces the coordinated water; the products are usually tetrammine or hexammine complexes (2) (see Coordination compounds). The hexahydrate of $Ni(BF_4)_2$ was found to be stable from 25 to 100°C; solubility also was determined to 95°C (86). At 120°C the solid decomposed slowly to NiF_2 with loss of HF, H_3BO_3, and H_2O.

3.1. 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 (87, 88) is patented. A typical cell for continous production consists of a polyethylene-lined tank with tin anodes at the bottom and a mercury pool (in a porous basket) cathode near the top (88). 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 HBF_4 is added to the top of the cell continuously. The direct reaction of tin with HBF_4 is slow but can be accelerated by passing air or oxygen through the solution (89). The stannic fluoroborate is reduced by reaction with mossy tin under an inert atmosphere. In earlier procedures, HBF_4 reacted with hydrated stannous oxide.

Anhydrous silver fluoroborate [1404-20-2] is made by the addition of BF_3 gas to a suspension of AgF in ethylbenzene (90). An $AgBF_4{\cdot}C_8H_{10}$ complex is precipitated with pentane and the complex is washed with pentane to give anhydrous $AgBF_4$.

3.2. Economic Aspects

Most fluoroborate solutions listed in Table 5 are manufactured by Atotech USA, Inc., General Chemical, Chemtec/Harstan, C.P. Chemical Co., and Fidelity Chemical Products. Prices are shown in Table 5.

3.3. 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 (91, 92). In the textile industry zinc fluoroborate is used extensively as the curing agent in applying resins for crease-resistant finishes (93). Emulsions of epoxy resins (94), polyoxy-methylene compounds (95), or aziridinyl compounds (96) with $Zn(BF_4)_2$ 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 (97), or the acrylic textiles can be coated with 20% $Zn(BF_4)_2$ which results in up to 5.5% added solids for a fire-resistant finish (98).

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 (99). The complexing tendency of olefins for $AgBF_4$ has led to the development of chemisorption methods for ethylene separation (100, 101). Copper(I) fluoroborate [14708-11-3] also forms complexes with olefins; hydrocarbon separations are effected by similar means (102).

The manufacture of linear polyester is catalyzed by Cd, Sn (103), Pb, Zn, or Mn (104) 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] (105). The caprolactam is polymerized to polyamide fibers using $Mn(BF_4)_2$ [30744-82-2] catalyst (106). 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 (107–109).

3.3.1. Electroplating

Metal fluoroborate electroplating(qv) baths (27, 110, 111) 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 HBF_4 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 (112, 113), Ni (113), and Co (113) 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 (113).

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 (114). Lead is plated alone or in combination with tin, indium, and antimony (115). 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 (116) (see Insulation, acoustic). Steel plates can be simultaneously electrocoated with lead and poly(tetrafluoroethylene) (117). Solder is plated in solutions containing $Pb(BF_4)_2$ and $Sn(BF_4)_2$; thus the lustrous solder-plated object is coated with a Pb–Sn alloy (118).

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