REFERENCE:

O. Ruff. Die Chemie des Fluors [Fluorine Chemistry], Springer, Berlin, 1920, p. 33.

Lead (IV) Fluoride

PbF_4

$$\underset{245.21}{PbF_2} + \underset{38}{F_2} = \underset{283.21}{PbF_4}$$

The apparatus described under BiF_5 (p. 202) contains an alundum boat used for fluorination of PbF_2 at 300°C. The F_2 is initially diluted with CO_2 or N_2, but its concentration in the gas mixture is slowly increased while the temperature is gradually raised to 500°C. The major portion of the PbF_4 remains in the boat in the form of 1-2 mm.-long needles.

After the fluorination is terminated, the boat with the PbF_4 is pulled into the glass cap placed on the reaction vessel, and the product is scraped out with a Ni wire. The solid drops into the glass ampoules, which are immediately sealed off.

PROPERTIES:

White crystalline substance, very sensitive to moisture, immediately discolors in air yielding brown PbO_2.

M.p. 600°C; d 6.7; tetragonal crystals.

REFERENCE:

H. v. Wartenberg. Z. anorg. allg. Chem. 244, 339 (1940).

Boron Trifluoride

BF_3

I.

$$\underset{125.92}{KBF_4} + 2\,\underset{139.28}{B_2O_3} = \underset{67.82}{BF_3} + \underset{197.38}{KF \cdot B_4O_6}$$

A mixture of 80 g. of dried or, preferably, melted KBF_4 and 30 g. of B_2O_3 is heated to about 600°C in an inclined iron tube (40 cm. long, 3 cm. diameter), which is sealed at one end. The other end of the iron tube is closed by a flange sealed with a copper gasket. An appr. 10-mm.-diameter iron tube is welded into an

opening in the flange and is connected to a drying tube filled with glass wool, which acts as a dust filter. The drying tube is in turn joined to a quartz or glass trap cooled in liquid nitrogen. The apparatus ends in a drying tube filled with freshly dried KF. The yield is 17 g. of BF_3. This can be purified by repeated fractional distillation.

II. $$\underset{658.92}{6\,NaBF_4} + \underset{69.64}{B_2O_3} + \underset{588.40}{6\,H_2SO_4} = \underset{542.56}{8\,BF_3} + \underset{720.36}{6\,NaHSO_4} + \underset{54.04}{3\,H_2O}$$

A mixture of 300 g. of $NaBF_4$, 50 g. of B_2O_3 and 300 ml. of concentrated H_2SO_4 is carefully heated in a one-liter flask provided with a ground-glass joint (see Fig. 133) until gas evolution starts. Only then can more heat be applied. The exit gas passes through a condenser, then through an absorption tube filled with B_2O_3 which has been interspaced with glass wool, and finally it is condensed in a trap at —196°C. A KF drying tube is placed at the end of the system in order to exclude moisture.

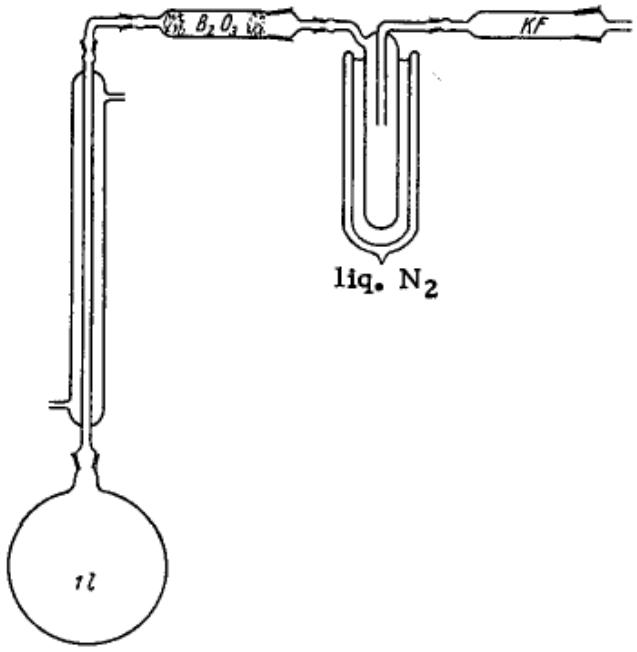

Fig. 133. Preparation of boron trifluoride.

The advantage of this method of preparation is that the residues are water soluble and the reaction vessel can be easily cleaned.

According to Ryss and Polyakova, the best BF_3 yield (80%) is obtained at 180°C with 105.9% sulfuric acid (oleum) in a 200% excess.

III. $$\underset{61.84}{H_3BO_3} + \underset{300.22}{3\,HSO_3F} = \underset{67.82}{BF_3} + \underset{294.24}{3\,H_2SO_4}$$

Concentrated H_2SO_4 is placed in an iron reaction vessel, which has one gas and two addition nozzles on top and one outlet nozzle

(with a valve) at the bottom. A solution of 20-25% boric acid in concentrated H_2SO_4 and HSO_3F is added at 85 to 135°C. The BF_3 is slowly liberated. The H_2SO_4 which accumulates may be removed from time to time at the bottom and may be used to dissolve the boric acid.

Further preparative methods: IV. Thermal decomposition of diazonium fluoroborates [G. Balz and G. Schiemann, Ber. dtsch. chem Ges. 60, 1186 (1927)].

V. A mixture of 40 g. of KBF_4, 8 g. of B_2O_3 and 120 ml. of concentrated sulfuric acid is heated to 270°C on a sand bath in a 300-ml. flask equipped with ground-glass joints [P. Baumgarten and H. Henning. Ber. dtsch. chem. Ges. 72, 1747 (1931)].

The older method for preparing BF_3 starting with CaF_2 is not recommended, since the yields are low and the product is contaminated with SiF_4.

The product is stored in glass containers over Hg or in steel cylinders.

Derivatives: $BF_3 \cdot (OC_2H_5)_2$ p. 786
$BF_3 \cdot NH_3$ p. 785
$BF_3 \cdot 2H_2O$ p. 784
$H[BF_2(OH)_2]$ p. 784
$n\text{-}C_4H_9BF_2$ p. 802

PROPERTIES:

Colorless, asphyxiating gas, fumes in moist air, thermally very stable.

M.p. −128°C, b.p. −101°C; t_{cr} −12.25°C; p_{cr} 50.2 atm. gage; d (liq.) (−128°C) 1.769; d (solid) (−150°C) 1.87.

Hydrolyzes in water to give H_3BO_3 and HBF_4. The gas attacks rubber. Rubber tubing and stoppers should therefore be avoided in apparatus used in its preparation.

REFERENCES:

I. W. Hellriegel. Ber. dtsch. chem. Ges. 70, 689 (1937).
II. H. S. Booth and K. S. Willson. J. Amer. Chem. Soc. 57, 2273 (1935); I.G. Ryss and Y.M. Polyakova. Zh. Obshch. Khim. 19 (81), 1596 (1949) (Chem. Zentr. 50. II. 1329).
III. U. S. Patent 2,416, 133.

Fluoroboric Acid

HBF_4

$$\underset{61.82}{H_3BO_3} + \underset{80.04}{4\,HF} = \underset{87.82}{HBF_4} + \underset{54.04}{3\,H_2O}$$

A slightly larger than stoichiometric quantity of H_3BO_3 is added in small portions to an ice-cooled iron reaction vessel containing

70-90% hydrofluoric acid. The reaction is highly exothermic. After the reaction is completed, the excess H_3BO_3 is allowed to settle out and the pure HBF_4 is decanted.

Fluoroboric acid is stored in glass containers.

PROPERTIES:

Colorless liquid, does not attack glass at room temperature. Decomposes on heating with water, forming oxyfluoroboric acids. Toxic and inhibits fermentation even when present in traces.

REFERENCES:

Mathers, Stewart, Housemann and Lee. J. Amer. Chem. Soc. 37, 1516 (1915).

F. Fichter and K. Thiele. Z. anorg. allg. Chem. 67, 302 (1910).

Sodium Fluoroborate

$NaBF_4$

$$\underset{123.64}{2\,H_3BO_3} + \underset{160.08}{8\,HF} + \underset{105.99}{Na_2CO_3} = \underset{219.63}{2\,NaBF_4} + \underset{126.1}{7\,H_2O} + \underset{44.0}{CO_2}$$

Boric acid (6.2 g.) is added, with cooling, to 25 g. of 40% hydrofluoric acid contained in a Pt dish. The mixture is left standing for six hours at room temperature, then cooled with ice, and 5.3 g of dry Na_2CO_3 is added. The solution is then evaporated until crystallization starts. The salt can be recrystallized from water, whereby large, beautiful single crystals can be obtained. The $NaBF_4$ is finally dried under vacuum.

SYNONYMS:

Sodium fluoborate, sodium borofluoride.

PROPERTIES:

Formula weight 109.815. Colorless salt; crystallizes in the anhydrous form as clear, orthogonal, stubby prisms. Anhydrous $NaBF_4$ does not etch glass. Readily soluble in water. Rhombic crystals, isodimorphous with $NaClO_4$.

REFERENCE:

G. Balz and E. Wilke-Dörfurt. Z. anorg. allg. Chem. 159, 197 (1927).

Potassium Fluoroborate

KBF_4

$$\underset{61.82}{H_3BO_3} + \underset{80.04}{4\,HF} + \underset{56.11}{KOH} = \underset{125.92}{KBF_4} + \underset{72.05}{4\,H_2O}$$

Boric acid (6.2 g.) is added to 25 g. of 40% hydrofluoric acid solution contained in an ice-cooled platinum dish. The solution is allowed to stand at room temperature for six hours. At the end of this period it is again chilled with ice, and 5N KOH solution is added with constant stirring until the color of methyl orange changes. Crystalline KBF_4 precipitates out at the same time. The mother liquor and subsequent water washings are decanted and the crystals dried under vacuum. The yield is 90%.

PROPERTIES:

White, crystalline salt, nonhygroscopic.

M.p. 530°C, d_4^{20} 2.505. Solubility in water (20°C) 0.45; (100°C) 6.3 g./100 ml. Dimorphous: rhombic-bipyramidal and cubic structures (trans. temp. 276-280°C).

REFERENCES:

D. Vorländer, J. Hollatz and J. Fischer. Ber. dtsch. chem. Ges. 65, 535 (1932).

Potassium Hydroxyfluoroborate

KBF_3OH

$$\underset{156.22}{2\,KHF_2} + \underset{61.84}{H_3BO_3} = \underset{123.96}{KBF_3OH} + \underset{58.1}{KF} + \underset{36}{7\,H_2O}$$

Technical grade KHF_2 (100 g.) is dissolved in 250 ml. of water contained in a polyethylene beaker. The K_2SiF_6 and the undissolved KHF_2 are filtered off after several hours of standing; the clear solution is placed in an ice-cold water bath and 40 g. of boric acid is added with stirring. Rapid dissolution occurs. Small crystals separate from the solution within an hour. They are suction-filtered on a fritted glass filter, washed with a small amount of ice-cold water and with 95% methanol solution and acetone. The salt is then dried at 120°C.

PROPERTIES:

Melts without decomposition. Less soluble in water than KBF_4. Yields no precipitate with nitron acetate; hydrolyzed by KOH