Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINE COMPOUNDS, INORGANIC, IRON

1. Iron(II) Fluoride

Anhydrous iron(II) fluoride [7789-28-8], FeF_2, is a white solid. The off-white to buff-colored appearance of the material is attributed to the partial oxidation of Fe^{2+} to Fe^{3+}. FeF_2 is highly stable and does not decompose when heated in the presence of nitrogen. It is sparingly soluble in water but the solubility can be increased by the addition of aqueous HF or any strong acid. Physical properties are listed in Table 1. FeF_2 holds great promise in the field of advanced magnets known as the iron–boron–rare-earth-alloy sintered magnets (1).

FeF_2 was first prepared by the action of gaseous hydrogen fluoride over $FeCl_2$ in an iron boat (2). The reaction of anhydrous $FeCl_2$, $FeCl_2{\cdot}4H_2O$, or $FeSO_4{\cdot}7H_2O$ and anhydrous HF in plastic reaction vessels such as vessels of polyethylene, polypropylene, or Teflon results in quantitative yields of very high purity FeF_2. The anhydrous salt has also been prepared from a solid-state reaction of a mixture of FeC_2O_4 and NH_4F (weight ratio 1:3) at 300°C and 13.3 Pa (0.1 torr) (3). Other methods of preparation are also available (4, 5).

Colorless crystals of iron(II) fluoride tetrahydrate [13940-89-1], $FeF_2{\cdot}4H_2O$, can be obtained by dissolving metallic iron or the anhydrous salt in hydrofluoric acid. The crystals of $FeF_2{\cdot}4H_2O$ are sparingly soluble in water and decompose to Fe_2O_3 when heated in air.

The only reported industrial application for FeF_2 is its use in rust removal solutions based on oxalic acid (6). The anhydrous salt is commercially available in 100 g to 5 kg lots from Advance Research Chemicals, Aldrich Chemicals, Cerac, Johnson/Matthey, PCR, and other suppliers in the United States. As of 1993, the prices varied between $500 to $700/kg.

Toxicity of iron(II) fluoride has not been determined. FeF_2 is shipped as a nonhazardous material in plastic containers. The ACGIH has adopted (1991–1992) a TWA value of 1 mg/m^3 for iron as Fe, and 2.5 mg/m^3 for fluorides as F^-.

2. Iron(III) Fluoride

Iron(III) fluoride [7783-50-8], FeF_3, is the most widely known fluoride of iron. It is light greenish (lime green) in color and the crystals have a rhombic structure. Physical properties are listed in Table 1.

Anhydrous FeF_3 is prepared by the action of liquid or gaseous hydrogen fluoride on anhydrous $FeCl_3$ (see Iron compounds). FeF_3 is insoluble in alcohol, ether, and benzene, and sparingly soluble in anhydrous HF and water. The pH of a saturated solution in water varies between 3.5 and 4.0. Low pH indicates the presence of residual amounts of HF. The light gray color of the material is attributed to iron oxide or free iron impurities in the product.

The most important industrial application of the iron(III) fluoride is in the manufacture of Fe–Co–Nd magnets. Other significant uses are as a hydrocracking catalyst (7), as a catalyst for the preparation of perfluoroacyl fluorides (8), as a catalyst for hydrorefining of lubricating oils (9), as a fluorinating agent

Table 1. Physical Properties of Iron Fluorides

Property	FeF_2	FeF_3
mol wt	93.84	112.84
density, g/cm^3	4.09	3.87
mp, °C	1100	1000[a]
bp, °C	1837	
C_p, J/(mol·K)[b]	68.12	+91.0

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

(10), for pin-hole prevention in cast iron (11), as a catalyst for preparation of xenon–fluorine compounds (12), burning rate control catalyst, as a catalyst for aromatization, dealkylation, and polymerization, and conversion of vinylidene chloride to the fluoride (13), and in the manufacturing of flame-retardant polymers (14). The industrial market for iron(III) fluoride varies from 2000 kg/yr to 30,000 kg/yr and 1993 prices ranged from $25 to $100/kg. FeF_3 is available from Advance Research Chemicals, Aldrich Chemicals, Morrita Chemicals of Japan, and also Russian and European producers.

3. Hydrated Salts and Other Compounds

Hydrated iron(III) fluoride [15469-38-2], $FeF_3{\cdot}3H_2O$, is easily prepared from yellow Fe_2O_3 and hydrofluoric acid. Dehydration of $FeF_3{\cdot}3H_2O$ produces oxyfluorides of iron.

In the presence of excess HF, complex ions such as $FeF^-;_4$ and $FeF^-;_6$ are formed in solution. Neutralization using a base such as NaOH produces $NaFeF_4$ [15274-99-4] and Na_3FeF_6 [20955-11-7], respectively. The latter is used as a fluorinating agent (15).

A mixed valency pale yellow crystalline iron pentafluoride heptahydrate, $FeF_5{\cdot}7H_2O$, is prepared by dissolving iron powder in 40% HF in the presence of air (16). No applications have been reported for this material.

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