FLUORINE COMPOUNDS, INORGANIC, TITANIUM

1. Titanium(III) Fluoride

Titanium trifluoride [13470-08-1], TiF_3, is a blue crystalline solid that undergoes oxidation to TiO_2 upon heating in air at 100°C (see Titanium compounds). In the absence of air, disproportionation occurs above 950°C to give TiF_4 and titanium metal. TiF_3 decomposes at 1200°C, has a density of 2.98 g/cm^3, and is insoluble in water but soluble in acids and alkalies. The magnetic moment is 16.2×10^{-24} J/T (1.75 μB).

Titanium trifluoride is prepared by dissolving titanium metal in hydrofluoric acid (1, 2) or by passing anhydrous hydrogen fluoride over titanium trihydrate at 700°C or over heated titanium powder (3). Reaction of titanium trichloride and anhydrous hydrogen fluoride at room temperature yields a crude product that can be purified by sublimation under high vacuum at 930–950°C.

Titanium trifluoride can be stored in tightly closed polyethylene containers for several years. Shipping regulations classify the material as a corrosive solid and it should be handled in a fully ventilated area or in a chemical hood. The ACGIH adopted toxicity values (1992–1993) for TiF_3 is as TWA for fluorides as F^- 2.5 mg/m^3.

This material is available from Advance Research Chemicals, Inc., Aldrich Chemical Company, Inc., Aesar, Johnson/Matthey, Cerac, PCR, and Pfaltz & Bauer in the United States, Fluorochem of the United Kingdom, and Schuchardt of Germany. Its 1993 price was approximately $500/kg. No commercial applications have been reported.

2. Titanium(IV) Fluoride

Titanium tetrafluoride [7783-63-3], TiF_4, has potential for use in dental hygiene products. It is used in infrared transmitting halide glass.

TiF_4 is a colorless, very hygroscopic solid and is classified as a soft fluorinating reagent (4), fluorinating chlorosilanes to fluorosilanes at 100°C. It also forms adducts, some of them quite stable, with ammonia, pyridine, and ethanol. TiF_4 sublimes at 285.5°C, and melts at temperatures $>400°C$. It is soluble in water, alcohol, and pyridine, hydrolyzing in the former, and has a density of 2.79 g/mL.

Titanium tetrafluoride may be prepared by the action of elemental fluorine on titanium metal at 250°C (5) or on TiO_2 at 350°C. The most economical and convenient method is the action of liquid anhydrous HF on commercially available titanium tetrachloride in Teflon or Kynar containers. Polyethylene reacts with $TiCl_4$ and turns dark upon prolonged exposure. The excess of HF used is boiled off to remove residual chloride present in the intermediates.

Titanium(IV) fluoride dihydrate [60927-06-2], $TiF_4 \cdot 2H_2O$, crystals can be prepared by the action of aqueous HF on titanium metal. The solution is carefully evaporated to obtain the crystals. Neutral solutions when heated slowly hydrolyze and form titanium(IV) oxyfluoride [13537-16-1], $TiOF_2$ (6). Upon dissolution in hydrogen fluoride, TiF_4 forms hexafluorotitanic acid [17439-11-1], H_2TiF_6.

The most promising application of titanium tetrafluoride is for use in topical applications for prevention of dental caries (7–13). It is being evaluated and compared to NaF, MFP, and SnF_2 used in these applications. The other use is in mixed optical halide glass (14–16), and in the preparation of fluorotitanates (17–19).

Total consumption of TiF_4 in both the United States and Europe is less than 500 kg/yr. TiF_4 is available from Advance Research Chemicals, Inc., Aldrich, Aesar, Johnson/Matthey, Cerac, PCR, and Pfaltz & Bauer of the United States, Fluorochem of the United Kingdom, and Schuchardt of Germany. Its 1993 price varied between $300 to $400/kg.

3. Fluorotitanates

Hexafluoroanions of Group 4 (IVB) are octahedral crystals that are quite stable in acidic media. Solutions having $pH > 4$ tend to hydrolyze forming the metal dioxides. All three hexafluoroacids are known, ie, hexafluorotitanic acid, hexafluorozirconic acid [12021-95-3], H_2ZrF_6, and hexafluorohafnic acid [12021-47-5], H_2HfF_6. These acids exist only in aqueous media in the presence of excess hydrofluoric acid. Alkali, alkaline-earth, and other metal salts of these acids, M_2XF_6, where $X = Ti$ and $M = Li$ [19193-50-1], Na [17116-13-1], K [16919-27-0], Rb [16962-41-7], Cs [16919-28-1], NH_4 [16962-40-6], and Tl [26460-00-4], have been isolated as stable solids at ambient temperatures (20). Maximum concentration of hexafluorotitanic acid is found to be 63% in the presence of 0.5% excess HF. Its salts, NH_4^+, Li^+, and Na^+ are quite soluble in water, whereas those of K^+, Rb^+, and Cs^+ are only slightly soluble.

Fluorotitanic acid is used as a metal surface cleaning agent, as a catalyst, and as an aluminum finishing solvent (see Metal surface treatments). Fluorotitanates are used in abrasive grinding wheels and for incorporating titanium into aluminum alloys (see Abrasives; Aluminum and aluminum alloys).

Although titanium compounds are considered to be physiologically inert (21), fluorides in general are considered as toxic above 3 ppm level and extreme care should be taken in handling large amounts of titanium salts as well as hexafluorotitanic acid. The ACGIH adopted (1992–1993) toxicity limits are as TWA for fluorides as F^- 2.5 mg/m^3.

The total U.S. consumption of H_2TiF_6 is 20 t/yr. The 1993 price varied between $2.80 to $7.50/kg depending on quantity and specifications. It is packaged in DOT approved polyethylene-lined drums and the salts in polyethylene-lined fiber board drums.

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