Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINE COMPOUNDS, INORGANIC, ZIRCONIUM

Three binary zirconium fluorides ZrF_2, ZrF_3, and ZrF_4, are known to exist. The most important compounds industrially are zirconium tetrafluoride, ZrF_4, and fluorozirconic acid [12021-95-3], H_2ZrF_6, and its salts (see Zirconium and zirconium compounds).

1. Zirconium Difluoride

Zirconium difluoride [7783-49-5], ZrF_2, has been isolated in rare gas–solid matrices (1). ZrF_2, prepared by Knudsen cell techniques, is not commercially available.

2. Zirconium Trifluoride

Zirconium trifluoride [13814-22-7], ZrF_3, was first prepared by the fluorination of ZrH_2 using a mixture of H_2 and anhydrous HF at 750°C (2). It can also be prepared by the electrolysis of Zr metal in KF–NaF melts (3). Zirconium trifluoride is stable at ambient temperatures but decomposes at 300°C. It is slightly soluble in hot water and readily soluble in inorganic acids. This compound is of academic interest rather than of any industrial importance.

3. Zirconium Tetrafluoride

Zirconium tetrafluoride [7783-64-4], ZrF_4, is one of the many important inorganic fluorides that have played a role in the development of heavy-metal fluoride glass (HMFG) technology (see Glass). Table 1 summarizes some of the physical properties of zirconium tetrafluoride. Zirconium tetrafluoride monohydrate [14956-11-3], $ZrF_4{\cdot}H_2O$, and the trihydrate [14517-16-9], $ZrF_4{\cdot}3H_2O$, also exist. The hydrated forms can be prepared by dissolving zirconium hydroxy carbonate, commonly known as basic zirconium carbonate, in aqueous hydrogen fluoride and evaporating the solution to dryness. This produces the trihydrate $ZrF_4{\cdot}3H_2O$. The monohydrate, $ZrF_4{\cdot}H_2O$, is prepared by removing two moles of water from the trihydrate under dynamic vacuum at 70°C. The monohydrate can also be prepared by dissolving the anhydrous salt in aqueous hydrofluoric acid and evaporating the solution to dryness.

The anhydrous salt is prepared by several methods, eg, by reacting $ZrCl_4$ with liquid anhydrous HF. It is necessary to use an excess of HF which also acts as a wetting agent. The reaction is instantaneous and is carried out in a polyethylene jar or carboy. When the evolution of HCl ceases, the material is transferred to a tray and dried under an atmosphere of nitrogen. By proper selection of equipment, purification of raw material, and drying conditions, materials of spectrographic purity can be produced (4).

Table 1. Properties of ZrF_4

Property	Value
mol wt	167.21
sublimation point, °C	912
specific gravity	4.54
solubility in water at 25°C	1.388
ΔH_f, kJ/mol[a]	−1911
ΔG_f, kJ/mol[a]	−1807
S, J/(mol·K)[a]	104.6
C_p, J/(mol·K)[a]	103.7

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

Other methods of preparation of anhydrous ZrF_4 include the decomposition of $(NH_4)_3ZrF_7$ [17250-81-6] at 297°C (5). NH_4F sublimes and leaves the flow reactor.

The principal application of ZrF_4 has been in the manufacture of HMFGs of which the most widely investigated is the system composed of Zr, Ba, La, Al, and Na, also popularly known as the ZBLAN glasses. This system has revolutionized the optics industry because of the significantly superior qualities of these glasses over conventional silica glasses. The theoretical transmission losses for fluoride glass fibers are calculated to be 0.001 dB/km at 3.2 μm and 0.005 dB/km at 3.5 μm (6) (see Fiber optics). Transmission loss rates have been observed as low as 0.65 dB/km (4). Fluoride glasses, unlike the silica glasses, are expected to transmit light in the range of 2–4 micrometers or in the infrared range. ZBLAN fibers transmit light at a 5 to 10 times lower optical loss than that of silica fibers, and can be used for long distance data transmission, for use in mid-ir and multispectral optical components, ir domes, laser windows, laser hosts, for medical applications such as surgery and cauterization, and for nuclear radiation resistant transmitting devices (6–16).

Other applications of zirconium tetrafluoride are in molten salt reactor experiments; as a catalyst for the fluorination of chloroacetone to chlorofluoroacetone (17, 18); as a catalyst for olefin polymerization (19); as a catalyst for the conversion of a mixture of formaldehyde, acetaldehyde, and ammonia (in the ratio of 1:1:3:3) to pyridine (20); as an inhibitor for the combustion of NH_4ClO_4 (21); in rechargeable electrochemical cells (22); and in dental applications (23) (see Dental materials).

High purity ZrF_4 is available in the United States from Advance Research Chemicals, Inc., Air Products and Chemicals, Inc., Johnson–Matthey/AESAR group, Aldrich Chemical, and EM Industries, Inc. Ultrahigh purity (99.999%) material is available only from Air Products and Chemicals, Inc. of Allentown, Pennsylvania. The price varies depending on the purity of the material from \$25/kg (99%) through \$250/kg (99.99%), to \$1500–2500/kg (99.999%). Consumption of ZrF_4 in the United States is less than 5000 kg/yr.

4. Fluorozirconic Acid and Fluorozirconates

Hexafluorozirconic acid [12021-95-3]], H_2ZrF_6, is formed by dissolving freshly prepared oxide, fluoride, or carbonate of zirconium in aqueous HF. This acid is produced commercially in a concentration range of 10 to 47%. The acid can be stored at ambient temperatures in polyethylene or Teflon containers without decomposition for at least two years. By neutralization of the acid, several stable fluorozirconates can be produced, such as $(NH_4)_2ZrF_6$ [16919-31-6], Na_2ZrF_6 [16925-26-1], K_2ZrF_6 [16923-06-8], Rb_2ZrF_6 [16923-95-8], and Cs_2ZrF_6, $CaZrF_6$ [30868-51-0]. The acid is regulated as a corrosive liquid NOS for shipping purposes (UN ID 1760) and packaging requires a corrosive label. The toxicity of zirconium compounds in general is represented by the TWA 5 mg/m^3 as Zr. The TWA for fluorides is 2.5 mg/m^3.

Hexafluorozirconic acid is used in metal finishing and cleaning of metal surfaces, whereas the fluorozirconates are used in the manufacture of abrasive grinding wheels, in aluminum metallurgy, ceramics industry, glass manufacturing, in electrolytic cells, in the preparation of fluxes, and as a fire retardant (see Abrasives; Metal surface treatments).

High purity hexafluorozirconic acid and its salts are produced by Advance Research Chemicals of the United States, and Akita and Moritta of Japan. The technical-grade green-colored material is supplied by Cabot Corp. of the United States. In 1993, the U.S. market for fluorozirconic acid was about 250,000 kg/yr; the world market was less than 500,000 kg/yr. A principal part of this production is consumed by the wool, garment, and upholstery industries. The 1993 price varied between $2.4 to $6.6/kg depending on the quality and quantity required. Potassium fluorozirconate [16923-95-8], K_2ZrF_6, is commercially important; the world market is about 750,000 kg/yr. The most important application is as a fire-retardant material in the wool (qv) industry, for the manufacture of garments, upholstery for aeroplane industry, and children's clothes (see Flame retardants). The 1993 unit price was between $5.0 and $6.6/kg.

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Related Articles

Fluorine Compounds, Inorganic, Introduction; Fluorine Compounds, Inorganic, Aluminum; Fluorine Compounds, Inorganic, Ammonium; Fluorine Compounds, Inorganic, Antimony; Fluorine Compounds, Inorganic, Arsenic; Fluorine Compounds, Inorganic, Barium; Fluorine Compounds, Inorganic, Calcium; Fluorine Compounds, Inorganic, Cobalt; Fluorine Compounds, Inorganic, Copper; Fluorine Compounds, Inorganic, Germanium; Fluorine Compounds, Inorganic, Halogens; Fluorine Compounds, Inorganic, Hydrogen; Fluorine Compounds, Inorganic, Iron; Fluorine Compounds, Inorganic, Lead; Fluorine Compounds, Inorganic, Lithium; Fluorine Compounds, Inorganic, Magnesium; Fluorine Compounds, Inorganic, Mercury; Fluorine Compounds, Inorganic, Molybdenum; Fluorine Compounds, Inorganic, Nickel; Fluorine Compounds, Inorganic, Nitrogen; Fluorine Compounds, Inorganic, Oxygen; Fluorine Compounds, Inorganic, Phosphorus; Fluorine Compounds, Inorganic, Potassium; Fluorine Compounds, Inorganic, Rhenium; Fluorine Compounds, Inorganic, Silver; Fluorine Compounds, Inorganic, Sodium; Fluorine Compounds, Inorganic, Tantalum; Fluorine Compounds, Inorganic, Tin; Fluorine Compounds, Inorganic, Titanium; Fluorine Compounds, Inorganic, Tungsten; Fluorine Compounds, Inorganic, Zinc