

Chapter 10

THE MODERN INORGANIC FLUORO-CHEMICAL INDUSTRY

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History

The seed of today's inorganic fluorochemical industry was planted during World War II when techniques were developed for the large-scale production of various inorganic fluorides. Basic raw materials such as fluorspar (CaF_2), anhydrous hydrogen fluoride (AHF) and elemental fluorine gas (F_2) became commercially available from companies such as General Chemical (Allied Chemical), E. I. duPont de Nemours and Co., I.C.I., Kali Chemie, Harshaw Chemicals, Pennsalt Corporation (Pennwalt), Montedison, Rhône Poulenc and Ugine Kuhlmann which also acquired know-how for the production, storage and distribution of the last two very corrosive and highly reactive materials.

In spite of the abundance of fluorspar and sulfuric acid, the basic raw materials for AHF, and the commitment of large European and North American companies, there was a limited demand for inorganic fluorine compounds. Only a few industrial applications existed such as the use of cryolite (Na_3AlF_6) and aluminum trifluoride (AlF_3) for the aluminum industry, and aqueous hydrofluoric acid as an etchant in the glass industry, in steel pickling and in the preparation of inorganic salts for soldering fluxes, etc.

The other reason for a dormant period in the inorganic fluorides industry was the general lack of suitable equipment for handling very corrosive and toxic materials such as HF and fluorine gas. Furthermore, there were only a few schools which trained people to handle these unusual raw materials.

The development of poly(ethylene) of unreactive fluoropolymers such as poly(tetrafluoroethylene), Teflon[®] (PTFE), tetrafluoroethylene hexafluoropropylene copolymer (Teflon[®] FEP), Kynar[™] polyvinylidene fluoride (PVDF) and super alloys such as Hastelloy C, Monel 400, Ilium G, Inconel 600, have played a very important role in the growth of the modern inorganic fluorochemicals industry. Today pumps, valves, reactors, centrifuges and gauges can be coated with any of the above polymeric materials or can be constructed out of the super alloys. As a result the corrosive materials are stored and transferred from one piece of equipment to another with the help of

semi- or fully-automatic control systems. The availability of these modern systems has made possible the safe transportation of anhydrous hydrogen fluoride, aqueous hydrogen fluoride, interhalogens and fluorine gas from one continent to another. It has become a normal routine to ship these corrosive materials safely and promptly. Fifty years ago no one would have dreamt of transporting 48% HF from Europe to South Africa, or from Japan to the U.S.A.

In the early 1950s, the inorganic fluorine industry was, on the one hand, expanding to meet defense and civilian needs and on the other hand the phosphate fertilizer industry was creating a troublesome surplus of fluorosilicic acid or was releasing large quantities of SiF_4 and HF into the atmosphere. Fluorosilicic acid, commercially known as fluosilicic acid, became such an intolerable burden to the fertilizer industry that it was being given away or was dumped into rivers, but times have changed; the modern inorganic fluorine industry is now one of the most advanced, safe and reliable industries, and it plays an important role in the betterment of our modern civilization.

Although it is beyond the scope of this chapter to cover and illustrate complete details of the modern inorganic fluorine industry, attempts will be made to describe the most important materials of current commercial interest.

The fluorspar industry

Introduction

The naturally-occurring mineral fluorspar, CaF_2 , is the principal source of fluorine. The other major fluorine sources are fluoroapatite, $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$, and natural cryolite, Na_3AlF_6 . The World production of fluorspar in 1985 was around 5 million metric tonnes. Mexico is the World's largest producer [1]. The second largest producer is the Republic of South Africa which has the largest reserves, about 30% of the World's total reserves. The other producing countries, (in order of importance) are U.S.S.R., Mongolia, People's Republic of China, Spain, France, Thailand, United Kingdom, Italy, Czechoslovakia, German Democratic Republic, Morocco, Kenya, United States, Brazil, Federal Republic of Germany and India.

Classification and uses

Fluorspar is classified according to its uses and purity. (i) *Acid-grade fluorspar* — used in the production of anhydrous hydrogen fluoride and aqueous hydrofluoric acid, is at a minimum 97% CaF_2 . Acid-grade, low arsenic fluorspar contains less than 50 ppm arsenic. (ii) *Ceramic grade* — this material is 85 - 96% CaF_2 and is used extensively by the ceramic industry to produce opaque enamels, for covering steel parts of appliances and fixtures. (iii) *Metallurgical grade* — also known as Met-Spar, is only 70 - 80% CaF_2 , and the least expensive fluorspar on the market. It is used by steel, alumi-

num, magnesium and nonferrous metal industries as a smelting flux to refine alloys and to dephosphorize and desulfurize metals. It is also used by the brick industry as an antiscumming agent, as a bonding agent for abrasive wheels and as an important ingredient in Portland cement to lower the clinkering temperature.

The quality of fluorspar can be upgraded by various techniques such as (i) hand-sorting, especially in countries where labor is very inexpensive, (ii) gravity separation by use of cone, drum and cyclone separators, and (iii) froth-flotation.

Hydrogen fluoride

History

This most essential raw material for the inorganic and organic fluorine industries was first made when Schwankhard of Nurnberg in 1670 etched glass with fluorspar and sulfuric acid; subsequent work identified hydrofluoric acid [2 - 4]. Frémy was the first to produce anhydrous hydrogen fluoride, AHF, from fluorspar and conc. sulfuric acid [5]. The present laboratory preparation of AHF is essentially the same as in Frémy's experiment (see Chapter 1, p. 17).

In spite of the early discovery of this very important chemical, there was no significant commercial usage except in glass etching, polishing and foundry scale removing until 1931, when the first bulk shipment of AHF was made by Sterling Products Company (later merged with Pennsalt Mfg. Co.) for use in the manufacture of chlorofluorocarbons to be introduced as refrigerants (the FreonsTM, developed by Midgley and Henne, see Chapter 4).

Major applications of AHF then developed such as its use as an alkylation catalyst for aviation gasoline, and in the manufacture of uranium tetrafluoride, fluoropolymers, lubricants and chlorofluorocarbons for pressurized packaging. The successful growth of these projects resulted in a major revolution for the chemical industry which currently uses over 1.7 million metric tonnes per year of AHF [6], of which 42% is used by the fluorocarbon industry, 34% in the aluminum industry, 5% for uranium hexafluoride, 5.5% in the glass industry, 4.5% in pickling and galvanizing, 5% as a solvent and a catalyst for the alkylation of aromatic and aliphatic hydrocarbons by the petroleum industry, and the remaining 4% (1.5×10^8 lb) in the synthesis of inorganic fluorides.

Manufacture

Commercial grade 99.9% hydrogen fluoride is made by reacting dry acid-grade fluorspar with concentrated sulfuric acid in a heated steel kiln or retort. Hydrogen fluoride containing less than 30% water does not react with carbon steel.

Hydrofluoric acid (aqueous HF) is prepared by diluting anhydrous HF with water or directly from the fluorspar-acid reactor without the elaborate purification steps necessary to obtain the 99.9% product. (NOTE: Acid is

always added to cold water.) Commercial grade hydrofluoric acid is made in the concentration range 48 - 70%; for concentrations below 70% it is shipped in 55 gallon drums with polyethylene liners. It is routinely shipped in lined tank cars, but above 70% concentration in steel cars. High-purity electronics grade hydrofluoric acid has less than 0.03 ppm As and Sb, 0.5 ppm Fe, and 0.1 ppm Pb. Price: 1985 bulk prices, for anhydrous hydrogen fluoride, were \$0.69 per lb; 70% aq. HF came at \$0.43 per lb, and electronic grade 49% aq. HF at \$0.62 per lb [7].

Physical properties

Anhydrous hydrogen fluoride is a colorless liquid at room temperature with a vapor pressure greater than 1 atm (122.9 MPa or 17.8 psi) [8]. It more closely resembles water and ammonia in its physical properties than it does the other hydrogen halides (b.p., 19.54 °C [9]; m.p., -83.37 °C [10]; liquid density 0.9576 g cm⁻³ at 25 °C [11]). It is polymeric, with hydrogen bonding [12] (see Chapter 3).

Chemical properties

Anhydrous hydrogen fluoride does not react with silver, nickel, monel, copper or aluminum as long as a moisture and oxygen-free environment is maintained.

Safety

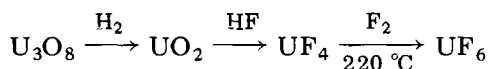
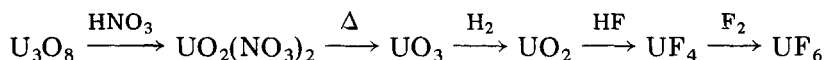
Anhydrous hydrogen fluoride and aqueous HF are extremely hazardous materials [13 - 15] (see Chapter 1).

Uranium hexafluoride

Introduction

Since the Manhattan Project, the production, enrichment and consumption of UF₆ have all become of great significance for nuclear weapons and power. Today atomic power plants are being operated in many countries: Austria, Argentina, Belgium, Brazil, Bulgaria, Canada, China (PRC), Cuba, Czechoslovakia, Egypt, Finland, France, East Germany (G.D.R.), West Germany (F.R.G.), Hungary, Italy, India, Pakistan, Philippines, Poland, Portugal, Rumania, South Africa, Spain, Sweden, Switzerland, Taiwan, United Kingdom, U.S.A., U.S.S.R. and Yugoslavia. These consumer countries depend on seven primary producers of UF₆ of which five are in the Western World.

Global need for UF₆ in 1985 was expected to be 30 000 metric tonnes of uranium as UF₆ (MTU), and is expected to be 40 000 MTU in 1990 and 45 000 MTU in 1995 [16]. These figures reflect annual consumption only. They do not include refuelling quantities or the first core fuel previously procured.

*Preparation**(A) Dry process**(B) Wet process**Properties*

Uranium hexafluoride is a colorless gas above 65 °C and a white solid at room temperature. The presence of other metallic impurities, such as chromium, produces a yellow color. It can be handled and stored in dry evacuated glass as shown in Fig. 10.1. It reacts with water to produce uranyl fluoride, UO_2F_2 , and HF. It is a good fluorinating reagent for both inorganics and halocarbons, e.g. it will oxidize AgF to AgF_2 and convert CCl_4 to CCl_3F .

Enrichment

Natural uranium ore, U_3O_8 , contains ^{238}U (99.275%) and ^{235}U (0.72%). Nuclear power plants need up to 5% enrichment and higher concentrations are essential for military purposes. Currently the enrichment of ^{235}U is carried out by gaseous thermal diffusion (GTDP) but recently a new technology, atomic vapor laser isotope separation (AVLIS), has been developed under the U.S. Department of Energy. The new technology, AVLIS, requires uranium metal as a feed material for enrichment instead of UF_6 and the recent decision to proceed with AVLIS technology for the enrichment of ^{235}U will affect U.S. fluorine producers by the year 2000.

Sulfur hexafluoride*Introduction*

Sulfur hexafluoride is widely used in electrical systems as an inert dielectric. During electrical discharge or arcing, sulfur hexafluoride may decompose into sulfur and fluorine, but the reaction is reversible and the dissociation products recombine. There are some secondary reactions which produce both solid and gaseous byproducts such as SF_4 , S_2F_2 , CuF_2 , WF_6 , etc., but these products are also good dielectrics so long as there is absence of moisture which would produce corrosive electrolytes such as HF and SOF_2 . To prevent the formation of harmful side-products, most arc-producing systems are protected with either activated alumina or molecular sieves.



Fig. 10.1. A sample of pure UF_6 sealed in glass is on the left-hand side and impure UF_6 containing chromium or nickel fluoride impurities is on the right-hand side.

Preparation

Sulfur hexafluoride was first prepared in 1902 by Moissan and Lebeau [17] who burned sulfur in an atmosphere of fluorine gas. Today it is manufactured by combining sulfur vapors with pure fluorine gas [18]. After preparation the gaseous mixture is scrubbed with NaOH to remove HF , F_2 and other impurities. Then it is heated at 400°C to decompose any disulfur decafluoride, S_2F_{10} , into SF_4 and SF_6 . The gaseous mixture is repassed through a NaOH tower followed by H_2SO_4 , BaO , P_2O_5 and activated alumina towers to remove SF_4 , moisture and entrained sulfuric acid.

Properties

Sulfur hexafluoride is a colorless, odorless, tasteless, nontoxic and nonflammable gas. It does not react with alkali hydroxide, ammonia or strong acids. Other properties are listed in Table 10.1.

TABLE 10.1

Physical properties of SF₆

m.p.	-50.5 °C
b.p.	-63.9 °C (sublimes)
critical temperature	45.5 °C
critical pressure	3.759 MPa (37.2 atm)
critical density	0.737 g cm ⁻³
gas density	6.602 g l ⁻¹
liquid density	1.88 g cm ⁻³ at -50.5 °C
solubility	sparingly soluble in water
dielectric constant (gas)	1.0024
dielectric constant (liquid)	1.81

Uses

The market of 6 - 8 million pounds annually arises principally from the high dielectric strength of sulfur hexafluoride [19 - 21] which gives it great importance in the electric power industry. Today it is extensively used in circuit breakers, high voltage coaxial cables, power substations and transformers (Fig. 10.2).

Since SF₆ is completely inert to glass, metals or sealing compounds it is used in three-pane glass windows (Fig. 10.3) to provide thermal insulation and to reduce noise transmission levels to 8 db or below. It is also used as an air flow tracer [22], as a refrigerant [23 - 25], in pneumothorax treatment [26], in loud speakers and in magnesium die-casting (Fig. 10.4).

Aluminum trifluoride

Introduction

Aluminum trifluoride is one of the most important commercial fluorides. Its manufacture consumes about 30% (U.S. 1.1×10^9 lb) of the total production of HF and plays a very important role in all domestic economies because of its use in aluminum production required for the automobile and housing industries. In addition to the extensive consumption of HF in making aluminum fluoride, an unknown amount (proprietary information) of the relatively less expensive H₂SiF₆ is used. This is generated as a byproduct from the phosphate fertilizer industry (see p. 207).

Manufacture

Wet process

Commercially, alumina hydrate, Al(OH)₃, is slowly added to a 15% hydrofluoric acid solution in a polyethylene or rubber-lined reactor. If the reaction temperature is kept below 25 °C, a soluble metastable α -AlF₃·3H₂O is produced which slowly and irreversibly changes to the less soluble, commercially usable β -AlF₃·3H₂O. If the reaction temperature rises to 95 °C, the

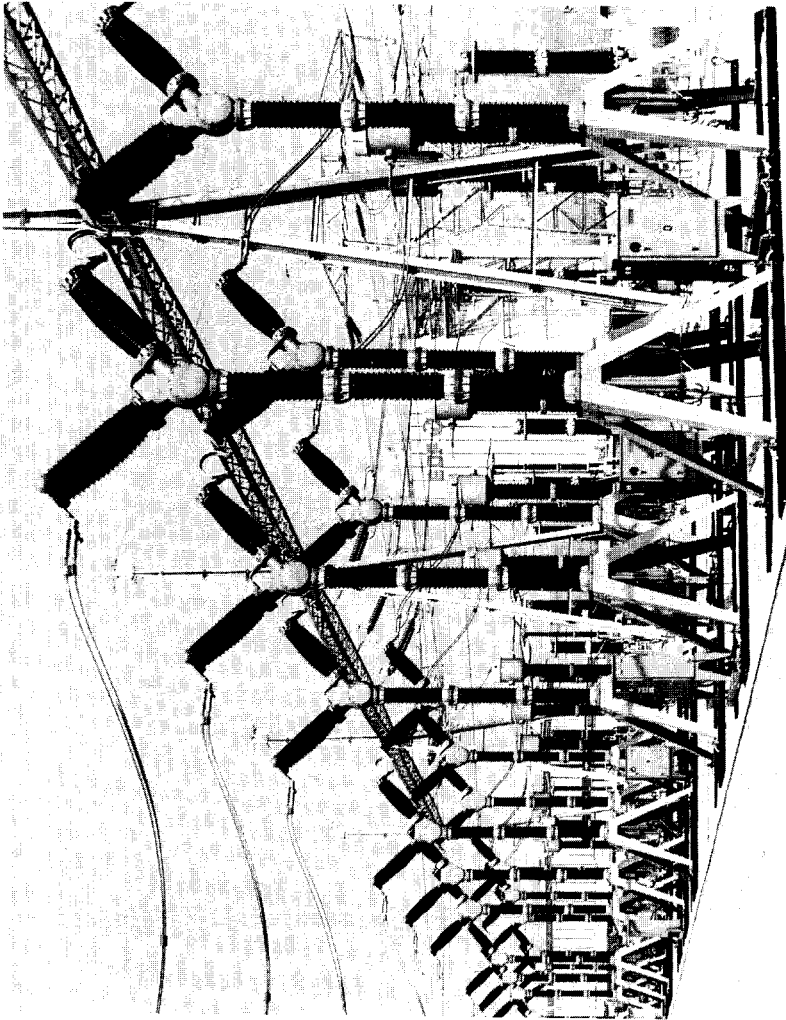


Fig. 10.2. 420 kV SF₆ outdoor-circuit breakers at Saint-Vulbas [photograph by courtesy of Kali-Chemie (U.S.A. branch)].

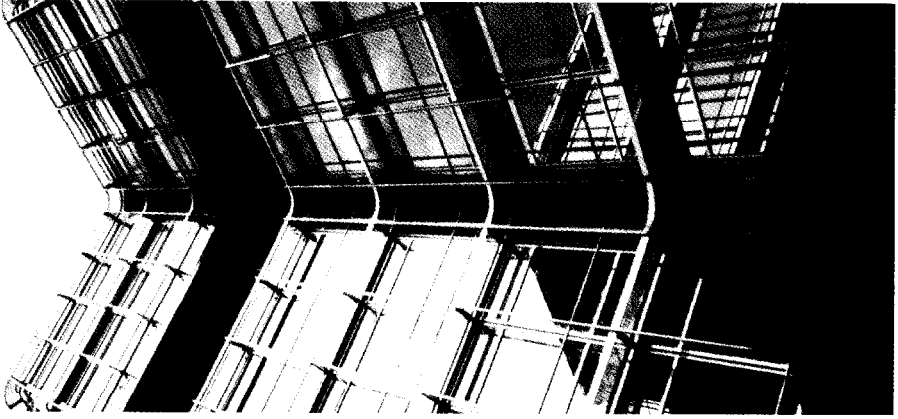


Fig. 10.3. SF₆-filled three-pane windows [photograph by courtesy of Kali-Chemie (U.S.A. branch)].

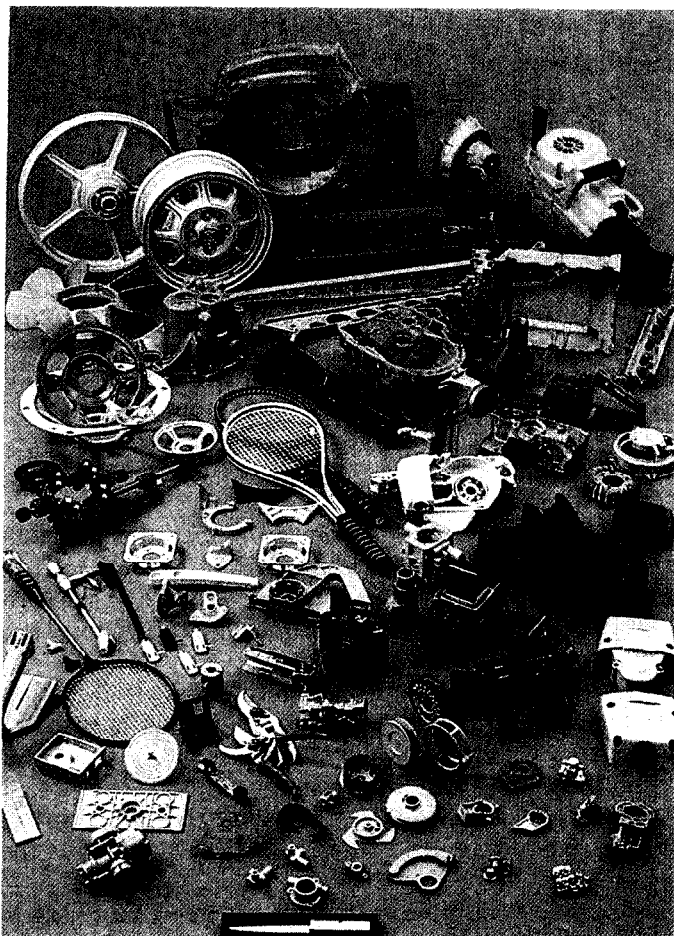


Fig. 10.4. Examples of SF_6 applied to cast-magnesium products [photograph by courtesy of Kali-Chemie (U.S.A. branch)].

α -form of $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ is converted into the β -form. The precipitate of $\beta\text{-AlF}_3 \cdot 3\text{H}_2\text{O}$ is digested at 95°C for several hours and then allowed to settle. The supernatant liquid is removed and the slurry is centrifuged and washed with cold water, dried and calcined to produce dry AlF_3 .

Dry process

Aluminum trifluoride may be advantageously made by a dry process if hydrogen fluoride is manufactured on-site. In this process, partially dehydrated alumina is treated at elevated temperature with gaseous hydrogen fluoride which enters at the bottom of a fluidized bed reactor. The temperature of the reaction zone is maintained at 590°C .

A typical composition of commercial grade aluminum trifluoride is given in Table 10.2.

TABLE 10.2

Typical composition of commercial grade AlF_3

AlF_3	90 - 92%
Al_2O_3	8 - 9%
SiO_2 (max.)	0.1%
iron as Fe_2O_3 (max.)	0.1%
sulfur as SO_2 (max.)	0.32%

Properties

Aluminum trifluoride is a white crystalline material, sparingly soluble in water and organic solvents. It is soluble to 15% in 40% HF but only to 2.8% in 65% HF.

Uses

Aluminum trifluoride is employed as a make-up ingredient in the molten cryolite (Na_3AlF_6)– Al_2O_3 bath used in aluminum reduction cells. A typical composition of the molten salt bath is 80 - 85% Na_3AlF_6 , 5 - 7% AlF_3 , 5 - 7% CaF_2 , 2 - 8% Al_2O_3 and 0.7% LiF with an operating temperature of 1000 °C.

Ideally fluorine is not consumed in the process but substantial quantities of fluorine are absorbed by the cell-lining. Fluorine is also lost to the atmosphere probably as NaAlF_4 which is always present as vapor above the molten cryolite baths. The modern efficient aluminum industry uses 24 kg (52.8 lb) of AlF_3 , and 21 kg (46.2 lb) Na_3AlF_6 , in producing one tonne of aluminum. Thus the bulk of the aluminum comes from Al_2O_3 which is fed intermittently into the cells.

Other relatively minor uses of aluminum fluoride are in ceramics, glass, glazes, enamels and catalysts, and in welding processes and coatings.

Cryolite

Introduction and preparation

Since the principal use of cryolite is in electrolytic cells for the production of aluminum metal, this fluorine compound is most commonly manufactured on the sites of aluminum plants. In the Bayer process, alumina is extracted from bauxite ore as a solution of sodium aluminate, NaAlO_2 ; gaseous HF from a sulfuric acid–fluorspar reaction is passed into the aqueous aluminate and the insoluble fluoride formed is filtered off and dried. Excess caustic is usually present. The product may be somewhat deficient in NaF if the aluminate liquor does not possess the requisite excess caustic.

The natural mineral which is of many colors (white, brown, black, purple or violet) has the exact stoichiometry $3\text{NaF} \cdot \text{AlF}_3$ (Na_3AlF_6), while the synthetic material is often deficient in sodium fluoride. However, the

synthetic product is a good substitute for the natural mineral which was once abundant in the mines of Ivigtut, Greenland. Today these mines are depleted and the World industry relies on synthetic cryolite [28].

A typical composition of cryolite prepared by the above methods is given in Table 10.3.

TABLE 10.3

Typical composition of cryolite

Na_3AlF_6 (min.)	91.4%
fluorine	48 - 52%
sodium	31 - 34%
aluminum	13 - 15%
alumina (Al_2O_3)	2 - 6%
SiO_2	0.14 - 0.3
CaF_2	0.4 - 0.9
Fe_2O_3	0.01 - 0.1
moisture	0.05 - 0.2

Properties

Synthetic cryolite is white in color. Its refractive index is close to that of water and as a result when it is immersed in water it resembles ice. Its melting point is 1012 °C. Its solubility in water is 0.042 g per 100 ml H_2O at 25 °C. It is insoluble in hydrochloric acid but soluble in hot concentrated NaOH solution. In the molten state it is in equilibrium with NaF and NaAlF_4 . Because of this dissociation, NaAlF_4 vapors are always present over molten cryolite baths.

Uses

The principal use of cryolite is in the manufacturing and refining of aluminum by electrolytic processes. Other uses include as a flux in the glass industry, as a filler for resin-bonded grinding wheels, in enamels, and as an insecticide for leaf-chewing insects on grape vines, citrus trees, beans and lettuce. It is also used as catalyst for olefin polymerization, in the surface coating of laser mirrors and in the manufacture of self-lubricating bearings.

Fluorosulfonic acid, fluorosulfuric acid

Introduction

Fluorosulfonic acid, HSO_3F , is an excellent solvent for many inorganic and organic compounds. It is a mild fluorinating agent and a very important catalyst in the petroleum industry because of its high acidity.

There are two producers of HSO_3F in the United States: Allied Corporation and E. I. duPont de Nemours Company, Inc. The latter manufac-

tures for internal use only, which leaves the Allied Corporation as the sole commercial source of HSO_3F . Allied Corporation markets HSO_3F in tank car quantities at \$1050 per metric tonne. The current World production is estimated to lie between 30×10^6 lb and 35×10^6 lb (13 000 to 16 000 metric tonnes) per annum.

Manufacture

An initial batch of fluorosulfonic acid is prepared by reaction of alkali-metal fluorides with chlorosulfonic acid [30], and is then used as a reaction medium to which stoichiometric amounts of AHF and SO_3 are added continuously. The fluorosulfonic acid formed is withdrawn continuously with some recycling to serve as the reaction medium [31, 32]. The role of the reaction medium is to provide close contact between HF and SO_3 and also to act as a heat sink for the exothermic reaction.

Properties

Fluorosulfonic acid is a colorless, mobile liquid which produces white fumes upon exposure to moist air or water vapors. It has a strong choking odor. Its chemical behavior and physical properties are intermediate between those of anhydrous HF and sulfuric acid as shown in Table 10.4.

TABLE 10.4
Comparison of the properties of HF, HSO_3F and H_2SO_4

Property	HF	HSO_3F	H_2SO_4
density/g ml ⁻¹	0.9576	1.0726	1.841
m.p./°C	-83.1	-88.98	10.36
b.p./°C	19.54	162.7	338
viscosity/cP	0.256 at 0 °C	1.56 at 25 °C	15.7 at 30 °C
specific conductance/ $\Omega^{-1} \text{ cm}^{-1}$	1.6×10^{-6}	1.085×10^{-4}	1.043×10^{-2}

When a strong Lewis acid such as SbF_5 is added to HSO_3F , its protonating power becomes greater than that of 100% H_2SO_4 . The solutions of Lewis acids in HSO_3F are known as super acids [29] (see chapter 14).

Uses

The patent literature contains many applications of HSO_3F . The petroleum industry uses HSO_3F as a catalyst for the alkylation of aliphatic and aromatic compounds [33 - 38], in polymerization of mono-olefins [39, 40], as an improved catalyst in the presence of Lewis acids such as SbF_5 , NbF_5 and TaF_5 [41 - 45], as a fluorinating agent in the synthesis of FClO_3 [46], BF_3 [47], SiF_4 [48, 49], acyl fluorides [50] and diazonium fluoro-sulfates, $\text{ArN}_2^+ \text{SO}_3\text{F}^-$ [51], and in the synthesis of alkali-metal fluoro-sulfates.

Hexafluorosilicic acid

Dentifrices

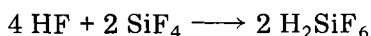
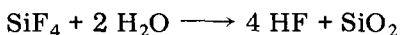
History

Hexafluorosilicic acid, H_2SiF_6 , commonly called fluorosilicic acid by industry, was once known as a troublesome byproduct of phosphate fertilizer plants. It was available almost free of charge at the production sites. Now it has become one of the important basic materials in the fluoridation of municipal water supplies to reduce the incidence of dental decay. It is also a valuable substitute for hydrogen fluoride in many applications.

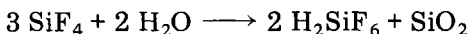
In 1931 it was shown that tooth decay was less frequent in areas where children received drinking water containing a low concentration of fluoride ions [52], and in 1945 the U.S. Public Health Service Department launched a controlled water fluoridation program. Under this program, the effect on tooth decay of 1 ppm fluoride ion concentration in drinking water was studied. Five years later, it became clear that controlled fluoridation of drinking water has the same desirable effect on limiting tooth decay as the naturally fluoridated water. As a result, fluoridation of potable water was recommended to reduce the incidence of dental caries. Today there are thousands of communities worldwide which are enjoying the benefits of water fluoridation. Fluoridation is frequently carried out using 20 - 30% concentrated hexafluorosilicic acid or dry salts such as NaF and Na_2SiF_6 .

Manufacture

Fluorosilicic acid is produced by the phosphate fertilizer industry as both HF and SiF_4 are byproducts of the reaction of sulfuric acid on phosphate rock. Environmental regulations require that these gases be collected by pollution control systems which are equipped with water scrubbers [53, 54]. Although these industries produce more SiF_4 than HF, the initial reaction of SiF_4 with water produces enough HF for the formation of H_2SiF_6 as shown by the equations



giving the overall reaction



Thus commercial H_2SiF_6 generally contains excess SiO_2 . The commercial grade H_2SiF_6 prepared in the water scrubbers has a concentration between 23 - 30%. Concentrated solutions of 40 - 45% strength can be prepared by distillation at room temperature under reduced pressure.

Properties

Fluorosilicic acid does not exist as the anhydrous compound; it is prepared as an aqueous solution from HF, SiF_4 and H_2O and does not have

precise physical properties. The boiling point of a 30.2% aqueous solution is 108.5 °C and the melting point is -35 °C. Acid of greater than 13.3% concentration corrodes glass. It forms several azeotropic mixtures.

Uses

As stated above, fluorosilicic acid is widely used in water fluoridation [55]. It is also used in the preparation of AlF_3 , alkali-metal fluorides and fluoro-silicates. Other applications include wood preservation, cement hardening, treatment of skin and hides, glass etching and in plaster.

Stannous fluoride, tin(II) fluoride

History

The discovery in 1950 by Dr. J. C. Muhler of Indiana University, that tin(II) ions add their own protective action against dental decay, led dentists into topical applications of SnF_2 solution. As a result, the Proctor and Gamble group developed a toothpaste (P & G Crest[®] containing 0.4% SnF_2) which was marketed as a therapeutic dental cream.

Crest[®] became so popular that it created a sudden market for several hundred tonnes of stannous fluoride per year. This lasted until 1980. In the mid-1970s the increased price of tin metal caused stannous fluoride to be replaced by sodium fluoride in a formulation superior to that originally used. The NaF active ingredient of Advanced Formula Crest[®] is given the trademark Fluoristat[®]; SnF_2 as an active ingredient is termed Fluoristan[®].

Preparation

Stannous fluoride was initially made commercially by solution of stannous oxide in aqueous hydrofluoric acid, and later by the patented process of reacting metallic tin with anhydrous hydrogen fluoride. The Ozark-Mahoning Company (Pennwalt Corporation) is the only current World manufacturer of stannous fluoride.

Properties

Stannous fluoride, SnF_2 , is a white crystalline salt which melts at 219.5 °C and boils at 850 °C. It is readily soluble in water and a 41.5% concentrated solution can be prepared at room temperature. It is also soluble in anhydrous and aqueous HF.

Uses

The major commercial use of SnF_2 is in dentifrices and other dental preparations.

Sodium monofluorophosphate, Na_2PO_3F

History

In 1950 the work of Shourie *et al.* [56] at the University of Rochester in New York State indicated that sodium monofluorophosphate, Na_2PO_3F ,

has a protective action on animal teeth, and the comparative study of Hayden [57] showing that sodium monofluorophosphate is approximately twice as effective as NaF in inhibiting acid production in a saliva-glucose mixture led investigators at the Colgate-Palmolive Co. to incorporate the safe and effective ingredient, $\text{Na}_2\text{PO}_3\text{F}$, in their toothpaste which is marketed worldwide as Colgate MFP[®].

Today several hundred tonnes of sodium monofluorophosphate are used annually in toothpaste and other dental preparations worldwide.

Preparation

$\text{Na}_2\text{PO}_3\text{F}$ is prepared commercially by fusion of sodium fluoride with sodium metaphosphate [58] at 650 °C.

Properties

Sodium monofluorophosphate is very soluble in water (42 g $\text{Na}_2\text{PO}_3\text{F}$ per 100 g solution). Dilute aqueous solutions of $\text{Na}_2\text{PO}_3\text{F}$ are stable indefinitely. Its melting point is 625 °C.

Uses

Sodium monofluorophosphate is used in toothpaste at a concentration of 0.76 wt.% to produce the desired fluoride level of 1000 ppm. Although a mechanism for its effectiveness in reducing dental caries is not clear, it can be assumed that the fluorophosphate ion replaces the hydroxyl group in apatite and produces fluoroapatite which is less soluble in mouth acids.

Alkali-metal fluorides

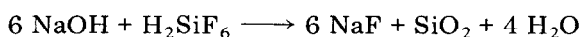
Introduction

Among the alkali-metal fluorides, sodium, lithium and potassium fluoride are produced commercially in bulk quantities, while cesium and rubidium fluorides are produced on a pilot-plant scale.

Sodium fluoride

Manufacturing and marketing

Alkali-metal fluorides may be prepared by the reaction of carbonates or hydroxides with dilute hydrofluoric acid. Nowadays, the bulk of sodium fluoride is prepared in Western Europe, Japan and the U.S.A. by reacting sodium hydroxide with inexpensive and readily available hexafluorosilicic acid.



This method for the production of NaF from H_2SiF_6 has been so successful that the old process via HF may become uncommercial. Because of this technology very high purity NaF is being sold in the U.S.A. at \$0.45 per lb F.O.B. buyer's destination, while the cost of raw materials alone in the HF

route is about \$0.50 per lb. Annual worldwide active consumption of NaF is not available, but can be estimated in the range of several million metric tonnes.

Properties

Sodium fluoride is a white crystalline powder, moderately soluble in water (4.2 g per 100 g H₂O), m.p. 992 °C and b.p. 1704 °C. In contact with concentrated acids it produces HF. Small doses of 25 - 50 mg can cause diarrhea and vomiting, and large doses (4 - 5 g) are fatal. In shipping, sodium fluoride is considered a poisonous chemical.

Uses

The principal uses of sodium fluoride are in the fluoridation of potable water supplies to reduce dental caries, and in the manufacture of sodium monofluorophosphate, vitreous enamels, wood preservation formulae, glues, coated papers, laundry sour, resmelting of aluminum, in fluxes and pickling stainless steel and chemicals for toothpaste formulations.

Lithium fluoride

Introduction

Lithium fluoride is the second most important alkali-metal fluoride due to its unique properties in respect of its solubility in water and polar solvents, and its chemical reactivity.

Manufacture

Lithium fluoride is prepared commercially by neutralizing hydrofluoric acid with lithium hydroxide or carbonate and filtering out the precipitates. On a small scale it can be prepared by reacting hydrofluoric acid or ammonium bifluoride solution with lithium chloride and nitrate [59].

Uses

The principal use of LiF is in the ceramic industry where it is employed to reduce firing temperatures and improve resistance to thermal shock. It is also used in bulk by the welding rod manufacturing industry, in substantial amounts in cryolite baths in the production of aluminum, in the electrolyte used for fluorine production to improve the wettability of carbon anodes and in the manufacture of prisms for IR and UV spectroscopy [60], and in X-ray monochromators. LiF is also used as a carrier in breeder reactors [61]. Its World consumption is *ca.* 500 000 lb per year.

Potassium fluoride

Anhydrous potassium fluoride is an important alkali-metal fluoride which is used for substituting halogens and oxygen-bonded groups of organic compounds.

Preparation

Potassium fluoride is prepared commercially by neutralization of H₂SiF₆ with KOH or by reacting HF with KOH or K₂CO₃. The aqueous

solution of KF is spray-dried or flaked on a heated drum. Potassium fluoride does not hydrolyze even at its melting point (857 °C). Anhydrous KF containing less than 100 ppm water can be prepared by heating to 200 °C.

Properties

Potassium fluoride is a very hygroscopic white crystalline powder, highly soluble in water (92.3 g KF per 100 g H₂O at 18 °C) and anhydrous HF (36.5 g per 100 g HF). It forms acid fluorides with AHF, such as KF·HF (m.p., 239 °C), KF·2HF (m.p., 71.7 °C) and KF·3HF (m.p., 65.8 °C). Potassium fluoride also forms two hydrates, KF·2H₂O and KF·4H₂O. The tetrahydrate is stable only below 17 °C, while the dihydrate starts losing water at 40 °C. The density of potassium fluoride is 2.48 g cm⁻³, m.p. 846 °C and b.p. 1505 °C. The fluorinating efficiency of KF depends upon the particle size, surface area, reaction temperature and the solvent used.

Uses

The bulk of potassium fluoride produced by the industry is used in the manufacture of fluxes, as electrolyte for fluorine cells, and in the fluorination of aromatic halides, carboxylic acid halides, haloesters, haloalcohols, alkyl halides and acyl halides.

Rubidium and cesium fluorides

Properties and uses

Although rubidium and cesium fluorides are more active as fluorinating agents than potassium fluoride, their uses are restricted on an industrial scale because of cost. These fluorides are only used in processes where other alkali-metal fluorides have failed. Cesium fluoride is used as a catalyst in the polymerization of fluoro-olefins. Demand for each of the reagents is less than a tonne per year.

Transition metal fluorides

Introduction

Although most of the 30 transition elements form two or more fluorides or metal complexes, only a few compounds, such as AgF₂, HgF₂, CoF₃, NbF₅, TaF₅, ReF₆ and WF₆ have been found of some industrial importance. The current worldwide market for these chemicals varies from less than 100 kg per year to several metric tonnes.

Cobalt trifluoride, silver difluoride and mercury difluoride

Cobalt trifluoride, silver difluoride and mercury difluoride are the reagents used in the fluorination of hydrocarbons. Mercury difluoride being toxic and very sensitive to moisture is used in selective fluorination only. Silver difluoride, in spite of being a more efficient fluorinating reagent than cobalt trifluoride [62], has limited use due to the high cost of silver.

Recently, several European and United States companies have been involved in exploring cobalt trifluoride technology to produce fluorocarbons to be used as blood substitutes, in vapor soldering technology, electronics, etching, etc.

Preparation

Cobalt trifluoride, mercury difluoride and silver difluoride can be prepared by the direct fluorination of the anhydrous chlorides, carbonates, oxides and low-valency metal fluorides.

Niobium and tantalum pentafluorides

The catalytic activities of niobium and tantalum pentafluorides have been extensively investigated by Siskin and coworkers [63, 64]. Their work shows that in the presence of AHF, they act as selective alkylation catalysts and promote the conversion of aromatics to alkyl aromatics, alkylating light paraffins with lower olefins, C_{2-5} , and hydrogenation of aromatic rings. The other important application of niobium and tantalum pentafluorides is in chemical vapor deposition (CVD). Both the fluoride salts have to compete with chlorides which are less expensive.

Preparation

Niobium and tantalum pentafluorides are prepared by the action of anhydrous hydrogen fluoride on metal powders or with metal pentachlorides. Current U.S. production of both salts is less than 500 kg per year.

Properties

Niobium and tantalum pentafluorides are snow-white crystalline powders, hygroscopic and soluble in water. They form stable complexes with alkali-metal fluorides, such as M_2NbF_7 and M_2TaF_7 . Their physical properties are listed in Table 10.5.

TABLE 10.5

Physical properties of niobium pentafluoride and tantalum pentafluoride

Property	NbF ₅	TaF ₅
color	white crystals	white crystals
density/g cm ⁻³	3.293	4.744
m.p./°C	73.0	96.8
b.p./°C	236	229.5

Rhenium and tungsten hexafluorides

Introduction

Of all the transition metal fluorides, rhenium and tungsten hexafluorides are the only two compounds for which there are no substitutes, and

they play a very important role in chemical vapor deposition (CVD), in which they are reduced by hydrogen at 550 - 750 °C under low pressure to produce a pure metal surface on a substrate [65]. Simultaneous depositions of rhenium and tungsten on a substrate by CVD improves its ductility and high-temperature resistance [68]. Tungsten CVD coatings are used as shields against X-ray or γ -radiation.

Preparation and properties

Rhenium hexafluoride — Rhenium hexafluoride is produced by reacting rhenium powder with elemental fluorine. The flow of fluorine is adjusted so that there is always an excess of rhenium powder present to avoid formation of rhenium heptafluoride. Rhenium hexafluoride is a yellow solid, m.p. 18.5 °C and b.p. 33.7 °C [66, 67]. Its liquid density is 6.157 g cm⁻³.

Tungsten hexafluoride — Tungsten hexafluoride is produced by reacting tungsten powder with elemental fluorine at 300 °C. There are no other side-products unless air or moisture enter the reaction system. Current U.S. production of tungsten hexafluoride is less than five tonnes per year.

Tungsten hexafluoride is a colorless gas which condenses to a pale yellow liquid. It melts at 2.5 °C at 420 mmHg pressure and boils at 17.5 °C. Its liquid density is 3.441 g cm⁻³ at 15 °C, and gas density is 12.9 g l⁻¹ [66].

Uses

The principal commercial use of rhenium and tungsten hexafluorides is in the production of rhenium–tungsten alloys by chemical vapor deposition technology (CVD). These alloys exhibit superconductivity with transition temperatures which are much higher than those alloys produced by arc-melting technology. CVD technology is also used in the manufacture of tubing, crucibles, nozzles and special parts used in space shuttles, which are exposed to high temperatures or corrosive atmospheres. It has been found that the joining of parts by diffusion bonding is superior to welding and that joints resist grain growth even at 1800 °C for 1200 h. Parts made by CVD can be readily machined. Tungsten surfaces produced by CVD have been claimed as very efficient solar-energy absorbers [117]. Tungsten hexafluoride is also used in providing hard tungsten carbide coatings on steel. Small amounts of tungsten hexafluoride are used in the electronics industry.

U.S. production of tungsten hexafluoride is less than 10 000 lb per year. In bulk, technical grade tungsten hexafluoride is sold at \$60.00 per lb and electronic grade at \$95.00 per lb.

Boron trifluoride, fluoroboric acid and fluoroborates

Boron trifluoride

Introduction

Boron trifluoride, a versatile industrial catalyst, was first prepared by Gay-Lussac and Thénard in 1809 by heating a mixture of boric acid and

fluorspar (CaF_2) at red heat [69]. Harshaw Chemical of Cleveland, OH, U.S.A., was the first company to announce commercial production of BF_3 in 1936 [70, 71]. In 1947, General Chemical Company, a Division of Allied Chemicals, developed a simple, continuous commercial process [72]. Currently, Allied Chemicals is the sole producer of boron trifluoride in the United States, although the Ozark-Mahoning Company, a subsidiary of Pennwalt Corporation, does produce small amounts of isotopically-enriched boron trifluorides.

Preparation

Currently, commercial grade 99.0% pure boron trifluoride is prepared by the action of fluorosulfuric acid on boric acid or boric oxide. The by-product, SO_3 , reacts with any moisture present in the system and keeps the product anhydrous.

Properties

BF_3 is a colorless gas which produces white smoke if discharged into the atmosphere. Its b.p. is -99.9°C , m.p. is -128.37°C [73] and gas density at STP is 3.0766 g l^{-1} . It is highly soluble in water to form an adduct $\text{BF}_3\cdot\text{H}_2\text{O}$, which slowly changes to $\text{H}^+ + [\text{BF}_3\text{OH}]^-$ [74]. It is slightly soluble in anhydrous HF and forms adducts with nitric and phosphoric acids, $\text{HNO}_3\cdot 2\text{BF}_3$ and $\text{H}_3\text{PO}_4\cdot\text{BF}_3$ [75]. It has a great tendency to form adducts with a variety of organic compounds, such as alcohols $\text{ROH}\cdot\text{BF}_3$, carboxylic acids $\text{RCOOH}\cdot\text{BF}_3$, acid anhydrides $(\text{ROC})_2\text{O}\cdot\text{BF}_3$, ethers $\text{R}_2\text{O}\cdot\text{BF}_3$, ketones $\text{R}_2\text{CO}\cdot\text{BF}_3$, aldehydes $\text{RCHO}\cdot\text{BF}_3$ and amines $\text{RNH}_2\cdot\text{BF}_3$. Virtually any molecule which has an electron-donating atom, such as oxygen, nitrogen or sulfur can react with the powerful electron acceptor boron trifluoride. It is soluble in organic solvents, such as C_2H_6 , C_3H_8 , C_6H_6 , CS_2 , CCl_4 , CHCl_3 , $\text{C}_6\text{H}_4\text{Cl}_2$ or $\text{C}_6\text{H}_5\text{NO}_2$.

Uses

Boron trifluoride, an excellent Lewis acid catalyst, is widely used in Friedel-Crafts and other chemical reactions [76, 77]. The most remarkable uses of boron trifluoride are in the alkylation of benzene with long-chain aliphatics to produce alkylbenzenes for the synthetic detergents industry. Boron trifluoride adducts with amines, phenols and aniline have widespread application as curing agents for epoxy resins, in the manufacture of alcohol-soluble phenolic resins and the dyeing of polyester fibers.

Boron trifluoride is used in the production of vinyl ether polymers and copolymers for the adhesives and surfactants industry. It is also used as an isomerization catalyst in the petroleum industry to produce gasoline and other important petroleum products.

The isotopic form of boron trifluoride $^{10}\text{BF}_3$ has a very important application in the nuclear energy industry as an absorber of thermal neutron flux in proportional neutron counters [103]. Isotopic boron trifluorides $^{10}\text{BF}_3$ and $^{11}\text{BF}_3$ also have important applications in ion implantation.

The worldwide consumption of BF_3 gas and etherates is in the multi-million pound range (ca. 10×10^6 lb).

Fluoroboric acid

Introduction

Fluoroboric acid, HBF_4 , does not exist in the pure state, but only as the solvated ion pair, $\text{H}_3\text{O}^+\text{BF}_4^-$. A typical commercial grade aqueous solution contains 48 - 50% fluoroboric acid to which a few per cent excess boric acid has been added to avoid HF fumes and HF burns. High purity solutions are available in the 40% concentration range only.

Manufacture

The most practical and economic commercial route for the preparation of fluoroboric acid is to react 70% hydrofluoric acid with boric acid, H_3BO_3 . Preparation by this route produces a solution which contains 48 - 50% HBF_4 .

Metaboric acid, HBO_2 , produces a 55 - 59% solution because of loss of water from the heat of the reaction, while reaction between boric oxide B_2O_3 and 70% HF will produce 59 - 62% HBF_4 solutions. Fluorosilicic acid reacts with boric acid to give fluoroboric acid.

The U.S. producers of fluoroboric acid are Allied Corporation, C.P. Chemical Company, Harshaw Chemicals, Harstan Chemicals Company and the Ozark-Mahoning Company (Pennwalt Corporation).

Properties

Aqueous fluoroboric acid is colorless, as strong relatively as nitric acid [78] but slowly hydrolyzing in a stepwise manner to $[\text{BF}_3\text{OH}]^-$, $[\text{BF}_2(\text{OH})_2]^-$, $[\text{BF}(\text{OH})_3]^-$ and finally to the starting materials, H_3BO_3 and HF [79]. Concentrated solutions of fluoroboric acid cannot be stored in glass indefinitely. Normally, BF_4^- ions do not coordinate to transition metals, but a few complexes do exist [80].

The specific gravity of 48% fluoroboric acid is 1.37 at 20 °C and the m.p. is less than -78 °C.

Uses

Fluoroboric acid is an essential chemical commodity extensively used in the manufacture of various fluoroborate salts and solutions. It is also used in the printing circuit board industry [81], in the polishing of aluminum, pickling of hot-rolled carbon steel, lead alloys and zinc die-casts, in the stripping of excess solder and metal deposition, in fluoroborate plating baths [82] for the treatment of metal surfaces, as an acid catalyst in the synthesis of polyol esters [83], and as a catalyst for the conversion of olefins to carboxylic acids by addition of CO and water [84]. The total consumption of 48% fluoroboric acid in the U.S.A. is about nine million pounds annually, and the current 1985 bulk price is \$0.91 per lb.

Fluoroborates

Introduction

Fluoroborates are important constituents of the fluoroboric acid baths used in electroplating and in the printed circuit board industry. Metal fluoroborates can be divided into five groups showing common chemical behavior or physical properties.

Group I	NOBF_4 , NO_2BF_4 , AgBF_4 , LiBF_4
Group II	NaBF_4 , NH_4BF_4 , KBF_4 , RbBF_4 , CsBF_4
Group III	$\text{Ba}(\text{BF}_4)_2$, $\text{Sr}(\text{BF}_4)_2$, $\text{Ca}(\text{BF}_4)_2$, $\text{Mg}(\text{BF}_4)_2$
Group IV	$\text{Pb}(\text{BF}_4)_2$, $\text{Sn}(\text{BF}_4)_2$, $\text{Zn}(\text{BF}_4)_2$, $\text{Cd}(\text{BF}_4)_2$
Group V	$\text{Cr}(\text{BF}_4)_3$, $\text{Mn}(\text{BF}_4)_2$, $\text{Fe}(\text{BF}_4)_2$, $\text{Co}(\text{BF}_4)_2$, $\text{Ni}(\text{BF}_4)_2$, $\text{Cu}(\text{BF}_4)_2$

The following discussion of fluoroborates will be according to the above classification.

Preparation, properties and uses

Group I – These fluoroborates are prepared on a laboratory or pilot-plant scale and require a water-free medium [85, 86]. Even under dynamic vacuum these salts decompose and produce BF_3 , HF, metal fluoride or oxides of nitrogen.

The fluoroborates of this group are very soluble in water and form conducting solutions in polar solvents. None of these fluoroborates is used in electroplating or the printed circuit board industry. Each fluoroborate has a specific application, e.g. silver tetrafluoroborate is used as a complexing agent for olefins and aromatics to obtain 99% pure olefins from a mixture of paraffins and acetylenes, and similarly to obtain high-purity cyclo-olefins and aromatics from cyclohexane [87, 88]. Anhydrous lithium tetrafluoroborate is extensively used as an electrolyte in lithium batteries [89] and NO_2BF_4 is an excellent nitrating agent for aromatics [90 - 94]. NOBF_4 reacts with aromatic amine hydrochlorides to produce diazonium tetrafluoroborates, which upon decomposition produce fluoroaromatics. It also reacts with methanol and produces methyl nitrate, and with aliphatic monoalkyl amines it produces monoalkylammonium tetrafluoroborates.

Group II – This group of fluoroborates is produced on a commercial scale from fluoroboric acid by reaction with hydroxides, carbonates, bicarbonates, fluorides, bifluorides or chlorides. Fluoroborate salts can be recovered from aqueous solution. Of this group, sodium and ammonium fluoroborates are soluble in water; the other fluoroborates KBF_4 , RbBF_4 and CsBF_4 , are practically insoluble. The properties of these fluoroborates are summarized in Table 10.6 [95 - 97].

Producers in the U.S.A. of these fluoroborates are Allied Corporation, Harshaw Chemicals, Kawecki-Berylco and the Ozark-Mahoning Company (Pennwalt Corporation).

Rubidium and cesium fluoroborates are produced on a small batch scale and are very expensive (\$500 per lb), while the other fluoroborates of

TABLE 10.6
Properties of Group II fluoroborates

Compound	Color	Melting point (decomposition temperature)/°C	Density/ g cm ⁻³	Solubility/ g per 100 g H ₂ O
NaBF ₄	white	384	2.47	108/26 °C
NH ₄ BF ₄	white	487	1.871	25/16 °C
CsBF ₄	white	555	3.2	1.6/17 °C
RbBF ₄	white	612	2.82	0.6/17 °C
KBF ₄	colorless	350	2.498	0.44/17 °C

this group are produced in several tonne quantities. The price of bulk fluoroborates varies from \$0.85 per lb to \$3.00 per lb, and depends upon the source of raw materials, purity and the quantity required.

Fluoroborates of this group are used in the preparation of fluxes required by metal-processing industries. The tendency of these fluoroborates to decompose at moderate temperatures as shown in Table 10.6, releasing BF₃ gas which inhibits the oxidation of metals, leads to their use in magnesium casting and heat treatment of aluminum alloys.

In the metal surface treatment process, in the molten state these fluoroborates dissolve the oxides of metals and help to clean the metal surface. Sodium and potassium fluoroborates are also used in the fabrication of grinding wheel and disk formulations to reduce the operating temperature [98 - 101]. They are also used as fire retardants for cotton and rayon [101], and in the preparation of etching solutions for the removal of exposed lead in printed circuit boards [102].

Group III — Fluoroborates of this group are also prepared by the action of carbonates, oxides or hydroxides on fluoroboric acid. They are produced as hydrates, Ba(BF₄)₂·2H₂O, Ca(BF₄)₂·2H₂O, Sr(BF₄)₂·4H₂O and Mg(BF₄)₂·6H₂O, which can be dehydrated completely to the anhydrous salts. Magnesium tetrafluoroborate is the least stable and will decompose to MgF₂. This magnesium fluoride has important applications in the television tube industry. The most important application of this group, particularly Ca(BF₄)₂, is in the isotopic separation of ¹⁰B from ¹¹B.

Group IV — The fluoroborates of this group are obtained by reacting metals, carbonates, hydroxides and oxides with fluoroboric acid. They are very soluble in water and form stable hydrates, and it is very difficult to obtain them as anhydrous salts. As a result, these fluoroborates are available in the form of 40 - 50% solutions of M(BF₄)₂ containing 1 - 2% excess fluoroboric acid to eliminate precipitation of metal fluoride or metal complexes. The solutions of these fluoroborates are colorless. The fluoroborates of tin and lead can also be prepared in electrolytic cells [104, 105].

In the U.S.A., the printed circuit board industry (PCB) is the largest consumer of these fluoroborates. Electroplating baths of these fluoroborate

solutions provide a uniform deposit of metal, controlled grain size, and improved brightness and smoothness because of their 'throwing power ability'. For plating out of alloys, such as solder, the percentage of M^{n+} ($n = 2, 3$) in the anodes should be about the same as the desired composition for the solder deposition. Most of the metal deposited comes from the anode and not the salts.

Other applications of these fluoroborates are as catalysts for curing a wide range of epoxy resins at ambient or elevated temperatures [106, 107]. Resins cured with $Zn(BF_4)_2$ are used in textiles for producing antcrease and antistatic fabrics, and in providing a fire-resistant finish to the fabric [108].

There is a multimillion pound market in the U.S.A., Europe and Asia for these fluoroborates.

Group V — These colored metal fluoroborates have a tendency to form stable octahedral hydrates, $ML_6(BF_4)_n$ where $n = 2$ (except Cr where $n = 3$) and $L = H_2O$. The water of hydration can be replaced by the other ligands, such as ammonia, *N,N*-dimethylacetamide and methanol.

These fluoroborates are also available as 40 - 50% solutions and can be made by reacting carbonates, or freshly prepared hydroxides and oxides in fluoroboric acid. These solutions also contain 1 - 2% excess boric acid to eliminate precipitation of the metal fluorides or complexes.

Major applications for these fluoroborates are in electroplating baths which provide deposits of superior corrosion resistance, low stress and a remarkable hardenability [109]. The worldwide annual market for these fluoroborates is of the order of multimillion pounds.

Halogen fluorides

Introduction

Chlorine, bromine and iodine form seven stable binary fluorides, ClF , ClF_3 , ClF_5 , BrF_3 , BrF_5 , IF_5 and IF_7 , when reacted with elemental fluorine. Chlorine pentafluoride is more reactive than elemental fluorine while IF_5 is the mildest fluorinating reagent of all the binary fluorides.

The halogen fluorides are stored as liquids in steel containers offering an advantage over gaseous fluorine which can only be stored as a gas in large steel cylinders at 400 psi pressure. Thus fluorine requires a very large number of steel cylinders, costly transportation and huge space for storage.

Only three halogen fluorides, bromine trifluoride, chlorine trifluoride and iodine pentafluoride, are of industrial significance. Strictly speaking only iodine pentafluoride has been found to be of commercial importance as a fluorinating reagent. The high reactivity of the other halogen fluorides leads to the spontaneous release of sufficient energy during fluorination to attack the carbon skeleton of the molecule and to disrupt C—C bonds. The energy release can result in explosion, fire and the destruction of equipment. A further drawback in the use of halogen fluorides as fluorinating reagents is

that they often introduce both halogens into the substrate and produce a complex mixture which is difficult to separate.

Preparation

The preparation of only the industrially important halogen fluorides is discussed here.

Bromine trifluoride — A commercial preparation of bromine trifluoride involves a gas-phase reaction between bromine and fluorine in such a way that the ratio of bromine to fluorine is maintained close to 1:3. On a batch scale this compound can be prepared in the liquid phase, where fluorine is added to liquid bromine at temperatures below 50 °C. The reaction temperature is maintained at 15 - 50 °C by circulating cold water around the reactor.

Chlorine trifluoride — The preparation of chlorine trifluoride is always accompanied by the formation of the stable compound, chlorine monofluoride, which can only be eliminated by precise temperature and fluorine flow rate control, and by allowing sufficient time for the reaction.

A commercial preparation requires a gas-phase reaction of chlorine with fluorine at 290 °C with the ratio of chlorine to fluorine being kept slightly less than 1:3 to promote a conversion of ClF to ClF₃. The retention time should be high to promote maximum conversion to chlorine trifluoride.

Iodine pentafluoride — A commercial preparation requires a non-reactive solvent to dissolve solid iodine prior to fluorination with gaseous F₂. It has been found that iodine pentafluoride is a suitable solvent for iodine. In a continuous process, approximately 1% iodine is dissolved in IF₅ and brought into a fluorination reactor. The iodine pentafluoride is continuously removed from the reactor to a receiving vessel where a small portion is withdrawn as product while the major portion is used as a solvent [110].

Properties

Bromine trifluoride — Bromine trifluoride is a yellow liquid, but the commercial grade is always amber to red, probably because of the presence of a small amount of bromine, or due to dissociation of unstable BrF formed during fluorination. The material has a melting point of 8.8 °C, a boiling point of 125.7 °C and a liquid density of 2.803 g cm⁻³ at 25 °C. It reacts violently with water and hydrocarbons.

Chlorine trifluoride — Chlorine trifluoride is a colorless gas, a white solid or a pale yellow liquid. It melts at -76.3 °C and boils at 11.75 °C. Its liquid density is 1.825 g cm⁻³ at its boiling point. Its fluorinating power is close to that of fluorine gas. It reacts violently with water and hydrocarbons.

Iodine pentafluoride — Iodine pentafluoride is a pale yellow liquid at room temperature. Its melting point is 8.5 °C, boiling point 102 °C and liquid density 3.252 g cm⁻³. Iodine pentafluoride is the least reactive of the halogen fluorides.

General properties

When halogen fluorides come into contact with a metal surface at ambient temperature for the first time they form a superficial protective

metal fluoride film (passive film) of low permeability which provides protection against further reaction up to a certain temperature. Beyond this the metal fluoride film will dissolve in halogen fluorides and the newly exposed surface will be attacked by halogen fluorides which may continue to react beyond control. Hence, reactors or storage vessels made out of mild steel, copper or nickel containing halogen fluorides should never be allowed to reach high temperatures. The halogen fluorides oxidize metals to the highest valency and produce fluorides accordingly. Thus, for example, ClF_3 will reach high temperatures [111]. The halogen fluorides oxidize metals to the highest valency and produce fluorides accordingly. Thus, for example, ClF_3 will react with cobalt, lead, silver and tin salts to produce CoF_3 , PbF_4 , AgF_2 and SnF_4 , respectively. These reactions are very useful and economical in regenerating fixed-bed fluorinating reagents used for the fluorination of hydro-

Uses

Chlorine trifluoride — The annual production of ClF_3 in the United States is several hundred metric tonnes. Most of this amount is consumed by the nuclear fuel processing industry to convert uranium metal to UF_6 . The other uses of ClF_3 are as oil-well tubing cutters, in the preparation of ClF , for the regeneration of fluorinating reagents in fixed-bed reactors, and in the laboratory scale preparation of niobium and tantalum pentafluorides.

Bromine trifluoride — Current U.S. production of bromine trifluoride is several metric tonnes per year and most of the product is used in oil-well tubing cutters. It can also be used for the substitution of bromine by fluorine in bromoethanes without the replacement of hydrogen [113].

Iodine pentafluoride — Iodine pentafluoride is the mildest fluorinating agent of all the halogen fluorides. It is easy to control fluorination reactions with IF_5 and to reduce losses due to oxidative fragmentation. The most important use of IF_5 is with perfluoro-olefins in the presence of SbF_5 which acts as a catalyst for IF addition. The yield of telomer exceeds 98% based on perfluoro-olefins [114].

The current U.S. annual production of IF_5 is several hundred metric tonnes which may increase by several times within a few years. Its current bulk price is \$25.00 per lb.

Nitrogen trifluoride

Introduction

Among all the two dozen or so nitrogen fluorine-compounds which exist in the gaseous and solid states, nitrogen trifluoride is the only one of commercial significance.

Nitrogen trifluoride is an inert molecule at room temperature. Its reactivity with organic compounds is very low at low temperatures but precautions must be exercised. Because of the danger and risk involved in the fluorination of organic compounds with NF_3 , it has found little use as a fluorinating reagent for hydrocarbons.

Preparation

Nitrogen trifluoride was first prepared by Ruff in 1928 [118]. Since then several methods have been reported [119 - 124]. A current commercial process [124] involves direct fluorination of ammonia in the presence of molten ammonium bifluoride. HF generated as a byproduct reacts with ammonia and forms ammonium bifluoride. In a specially designed reactor (Air Products Co.), gaseous fluorine is brought into contact with molten ammonium bifluoride which acts as a heat and ammonia transport medium. This process is safer than the earlier electrolytic process [123] which generated both NF_3 and H_2 , and required extensive dilution of gas streams with N_2 to avoid explosions in the electrolytic cells.

Nitrogen trifluoride produced by the current process [124] is 98.6% pure. It contains small amounts of impurities such as N_2 , O_2 , CF_4 , SF_6 and N_2O , the impurities other than the nitrogen compounds being derived from the fluorine gas.

Properties

Nitrogen trifluoride is a noncorrosive gas at room temperature, and can be stored in carbon steel, copper, nickel or aluminum containers so long as the storage temperature remains below 70°C . The presence of moisture or HF promotes corrosion of these metals and must be avoided. High-purity nitrogen trifluoride is a colorless and odorless gas, but the commercial grade material has a musty and choking smell. It is very toxic with a threshold value of 30 mg m^{-3} or 10 ppm.

Nitrogen trifluoride is a very mild fluorinating agent below 35°C ; above this temperature its reactivity is increased substantially. It has a melting point of -206.8°C and a boiling point of -129.0°C [125]. Its liquid density is 1.533 g cm^{-3} and it is only slightly soluble in water.

Other physical properties of NF_3 have been extensively described by Anderson *et al.* [126].

Uses

The most significant use of nitrogen trifluoride is as a fluorine source for HF/DF high-energy chemical lasers [127]. Small amounts of NF_3 are used in the production of N_2F_4 and perfluoro-ammonium metal salts [128 - 132]; the latter are also used in HF/DF high-energy chemical lasers.

Air Products and Chemicals, Inc. is the chief commercial producer in the United States. Its current production is below 20 metric tonnes per annum and the 1985 price was \$165.00 per lb.

Antimony fluorides

Antimony pentafluoride

Preparation and properties

Antimony pentafluoride, SbF_5 , is a colorless, hygroscopic, very viscous liquid at room temperature. Its melting point is 7°C and boiling point is

142.7 °C with a density of 3.145 g cm⁻³ at 15.5 °C. It is a moderate fluorinating agent, spontaneously reacting with water and forming a dihydrate, SbF₅·2H₂O. This dihydrate reacts violently with additional water and then forms a clear solution.

Antimony pentafluoride can be prepared by refluxing a mixture of SbCl₅ and HF in an aluminum reactor. Currently, it is produced by the direct fluorination of SbF₃ at 300 °C. In this process antimony trifluoride is sublimed and the vapors are brought into contact with gaseous fluorine. The product, SbF₅, is distilled.

Use

The only significant commercial use of antimony pentafluoride is as a catalyst in the manufacture of telomers [114]. It is also used for the saturation of double bonds in straight-chain olefins, cyclo-olefins and aromatic rings [133 - 135], and in the fluorination of hydrocarbons.

The annual production of antimony pentafluoride in the United States is about 15 000 lb and the 1985 price was \$30 per lb for large quantities.

Antimony trifluoride

Preparation and properties

Antimony trifluoride is a hygroscopic, white solid which is very soluble in water, hydrofluoric acid and polar solvents such as acetone, methyl alcohol, etc. It acts as a very mild fluorinating reagent and does not react efficiently if used alone. However, in the Swarts reactions [136] (SbF₃ + Cl₂, SbF₃ + Br₂, SbF₃ + SbCl₅) its effectiveness is immensely increased.

It is easily prepared by dissolving Sb₂O₃ in aqueous HF (55% or greater concentration) followed by evaporation to dryness.

Uses

The only significant commercial use of antimony trifluoride is in the preparation of SbF₅. It is no longer used in the Swarts reactions to prepare hydrocarbons due to the development of alternative routes which involve the direct use of anhydrous hydrogen fluoride.

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