FLUORINE COMPOUNDS, INORGANIC, HYDROGEN

1. Introduction

Hydrogen fluoride [7664-39-3], HF, is the most important manufactured fluorine compound. It is the largest in terms of volume, and serves as the raw material for most other fluorine-containing chemicals. It is available either in anhydrous form or as an aqueous solution (usually 70%). Anhydrous hydrogen fluoride is a colorless liquid or gas having a boiling point of 19.5°C. It is a corrosive, hazardous material, fuming strongly, which causes severe burns upon contact. Rigorous safety precautions are the standard throughout the industry, and in practice hydrogen fluoride can be handled quite safely.

Although it was known in the early nineteenth century, commercial use of hydrogen fluoride was limited. All early production was as aqueous solutions for uses such as glass etching, foundry scale removal, and production of chemicals such as sodium fluoride and sodium bifluoride. Some hydrogen fluoride was also produced for captive use in aluminum manufacture. Production of anhydrous hydrogen fluoride began in the early 1930s, but the demand at that time was limited to the small market for chlorofluorocarbons (see FLUORINE COMPOUNDS, ORGANIC).

World War II brought a revolution in the HF field. The need for high octane aviation fuels (see AVIATION AND OTHER GAS TURBINE FUELS), the birth of the nuclear industry requiring uranium hexafluoride (see URANIUM AND URANIUM COMPOUNDS), and the rapid growth of the chlorofluorocarbon market all contributed to a steadily rising demand for hydrogen fluoride, especially in the anhydrous form. Whereas earlier anhydrous production had been solely via distillation of aqueous HF, technology emerged allowing direct production of anhydrous hydrogen fluoride.

2. Properties

2.1. Physical Properties.

Physical properties of anhydrous hydrogen fluoride are summarized in Table (1). Figure (1) shows the vapor pressure and latent heat of vaporization. The specific gravity of the liquid decreases almost linearly from 1.1 at −40°C to 0.84 at 80°C (4). The specific heat of anhydrous HF is shown in Figure (2) and the heat of solution in Figure (3)

Table (2) summarizes the properties of the hydrogen fluoride–water system. The freezing and boiling point curves of this system are shown in Figures (4) and (5), respectively. Figure (6) gives the partial pressures of HF and H_2O in aqueous HF solutions. The specific gravity of the solutions at various temperatures is shown in Figure (7). Specific conductivity of this system is given (27,28).

Hydrogen fluoride is unique among the hydrogen halides in that it strongly associates to form polymers in both the liquid and gaseous states. At high temperatures or low partial pressures, HF gas exists as a monomer. At lower temperatures and higher partial pressures hydrogen bonding leads to the formation of chains of increasing length, and molecular weights of 80 and higher are observed. Electron diffraction study of the gas (29) has shown the hydrogen

HF, wt %	Conductivity at 0°C, $(\Omega \cdot \text{cm})^{-1}$
70	7.9×10^{-1}
80	7.1×10^{-1}
85	6.3×10^{-1}
90	4.9×10^{-1}
92.5	3.8×10^{-1}
95	2.5×10^{-1}
96	1.95×10^{-1}
97	1.04×10^{-1}
98	9.4×10^{-2}
99	5.6×10^{-2}
99.5	3.4×10^{-2}
99.75	1.8×10^{-2}
99.9	5.7×10^{-3}
99.95	2.8×10^{-3}
100	$<1.6 \times 10^{-6}$

to fluorine distances to be about 0.10 nm and 0.155 nm, the F—H···F distance to be 0.255 nm, and the polymer to have a linear zig-zag configuration. The angle H—F—H is reported to be about 120°. Monomeric HF has an H · F distance of 0.0917 nm. Cyclical polymers (possibly H_6F_6) also probably occur. In general, polymers of differing molecular weights are present in equilibrium at a given temperature and pressure, and an average molecular weight encompasses many different actual molecules. The apparent molecular weight of anhydrous HF vapor is shown in Figure 8

This high degree of association results in highly nonideal physical properties. For example, heat effects resulting from vapor association may be significantly larger than the latent heat of vaporization (Fig. 9). Vapor heats of association (ΔH_{assoc}) for HF to $(\text{HF})_n$ per mole of $(\text{HF})_n$ are as follows. To convert kJ to kcal, divide by 4.184.

n	$-\Delta H_{\text{assoc}}$, kJ
2	33.0
3	67.4
4	101.7
5	133.9
6	167.4
7	198.7
8	224.3

2.2. Chemical Properties.

Hydrogen fluoride, characterized by its stability, has a dissociation energy of 560 kJ (134 kcal), which places HF among the most stable diatomic molecules. Hydrogen fluoride is, however, highly reactive, and it has a special affinity for oxygen compounds, reacting with boric acid to form boron trifluoride and with sulfur trioxide and sulfuric acid to form fluorosulfonic acid. This last reaction demonstrates the dehydrating power of anhydrous hydrogen fluoride. HF belongs to the only class of compounds that readily react with silica and silicates, including (qv). With organic compounds, HF acts as a dehydrating agent, a fluorinating agent, a polymerizing agent, a catalyst for condensation reactions, and a hydrolysis catalyst. Hydrogen fluoride reacts with alcohols and unsaturated compounds to form fluorides and with alkylene oxides to give alkylene fluorohydrins.

The strong catalytic activity of anhydrous hydrogen fluoride results from the ability to donate a proton, as in the dimerization of isobutylene (see BUTYLENES):

$$\begin{aligned}\mathrm{CH_2{=}C(CH_3)_2 + HF} &\rightarrow \mathrm{(CH_3)_3C^+ + F^-}\\ \mathrm{(CH_3)_3C^+ + CH_2{=}C(CH_3)_2} &\rightarrow \mathrm{(CH_3)_3C - CH_2C^+(CH_3)_2} \rightarrow\\ &\quad \mathrm{(CH_3)_3CCH{=}C(CH_2)_2 + H^+}\end{aligned}$$

Anhydrous hydrogen fluoride is an excellent solvent for ionic fluorides (Table 3). The soluble fluorides act as simple bases, becoming fully ionized and increasing the concentration of HF_2^-. For example,

$$\mathrm{HF + KF \rightarrow K^+ + HF_2^-}$$

Because of the small size of the fluoride ion, F^- participates in coordination structures of high rank. Tantalum and niobium form stable hexafluorotantalate and hexafluoroniobate ions and hydrogen fluoride attacks these usually acid-resistant metals. Hydrogen fluoride in water is a weak acid. Two dissociation constants are

$$K_1 = \frac{[H^+][F^-]}{[HF]} = 6.46 \times 10^{-4}\ M$$
$$K_2 = \frac{HF_2^-}{[HF][F^-]} = 5 \text{ to } 25\ M$$

Whereas hydrogen fluoride is a fairly weak acid as a solute, it is strongly acidic as a solvent. As the concentration of hydrogen fluoride increases in aqueous mixtures, the system becomes more acidic, with water acting as a very strong base. In dilute aqueous solution, an isolated hydrogen fluoride molecule donates a proton to an aggregate of water molecules and forms an aquated fluoride ion. When small amounts of water are present in the system, a proton is transferred to an isolated water molecule from polymeric hydrogen fluoride. The fluoride ion thus formed is part of a stable polymeric anionic complex. This difference in the solvation of the fluoride ion at the extremes of composition in the $H_2O{-}HF$ system is probably the principal factor affecting the ease of proton transfer (14).

For anhydrous hydrogen fluoride, the Hammett acidity function H_0 approaches -11. The high negative value of H_0 shows anhydrous hydrogen fluoride to be in the class of superacids. Addition of antimony pentafluoride to make a

3 M solution in anhydrous hydrogen fluoride raises the Hammett function to −15.2, nearly the strongest of all acids (34).

3. Manufacture

3.1. Raw Materials. Essentially all hydrogen fluoride manufactured worldwide is made from fluorspar and sulfuric acid, according to the reaction:

$$CaF_2(s) + H_2SO_4 \rightarrow CaSO_4(s) + 2\ HF(g)$$

Generally, yields on both fluorspar and sulfuric acid are greater than 90% in commercial plants.

Fluorspar. A typical acid-grade fluorspar analysis gives:

Component	Composition, wt %
calcium fluoride	97.0
silica	0.7
calcium carbonate	1.0
organic (as carbon)	0.1
sulfur	
total	0.02
sulfide	0.01
phosphorus pentoxide	0.02
chloride, total	0.02

Also present are 0.3 wt % mixed metal oxides (R_2O_3) and 5 ppm of arsenic. Impurities in fluorspar may affect yield, plant operability, or product quality.

Silica. Silica, which has the greatest impact on yield losses, reacts with HF and is discharged from the manufacturing process as H_2SiF_6. Yield losses can be calculated based on the chemical stoichiometry:

$$SiO_2 + 3\,H_2SO_4 + 3\,CaF_2 \rightarrow H_2\,iF_6 + 2\,H_2O + 3\,CaSO_4$$

or

$$6\,HF + SiO_2 \rightarrow H_2\,SiF_6 + 2\,H_2O$$

Calcium fluoride loss is equal to 3.9% for each 1% silica; sulfuric acid loss is equal to 4.9% for each 1% silica.

Mixed-Metal Oxides. Generally, iron oxide is the principal component of mixed-metal oxides. These affect the sulfuric and oleum consumption in HF production.

$$R_2O_3 + 3\,H_2SO_4 \rightarrow R_2(SO_4)_3 + 3\,H_2O$$

Sulfuric acid loss is approximately 1.84% H_2SO_4 for each percentage of R_2O_3. Oleum consumption is increased to consume the water that is formed. The metal sulfates are more stable than metal fluorides under furnace conditions and are discharged from the process with the residue.

Calcium Carbonate. Calcium carbonate, like R_2O_3, affects sulfuric and oleum consumption in the HF process. Sulfuric acid loss is approximately 0.98% H_2SO_4 for each percentage of $CaCO_3$. The carbon dioxide evolved by the reaction increases the noncondensable gas flow, and because it carries HF, contributes to yield losses in the vent stream.

Magnesium Oxide. Magnesium oxide behaves in a similar manner to other metal oxides. However, most spars contain practically no magnesium oxide, so it does not affect yield loss or plant operation.

Organic Carbon. Organic materials interfere with plant operation because these compounds react with sulfuric acid under furnace conditions to form sulfur dioxide. There is a reducing atmosphere in the furnace which may reduce sulfur dioxide to elemental sulfur, which results in sulfur deposits in the gas handling system.

Total Sulfur and Sulfide Sulfur. Total sulfur is predominately in the form of metal sulfate, and because sulfates act as inerts, these materials have little impact on the process. Sulfide sulfur compounds, on the other hand, react and leave the furnace as a sulfur vapor, which may deposit in the gas handling system. A possible mechanism for this is the partial reaction of SO_2 to H_2S, followed by

$$2\,H_2S + SO_2 \rightarrow 3\,S + 2\,H_2O$$

Phosphorus Pentoxide. Phosphorus compounds form PF or POF compounds in the furnace. Some may be hydrolyzed to higher boiling forms in downstream process operation. Some of the phosphorus compounds do appear in the final product. This is objectionable to some users.

Chloride. Chloride is known to significantly increase the rate of corrosion in acidic fluoride media. The level of chloride that can be tolerated in the HF process before corrosion hinders plant operation is quite low.

Arsenic and Boron. Arsenic and boron form volatile fluorides which are difficult to separate from high purity HF. Special equipment and techniques must be used to remove the arsenic.

Sulfuric Acid. Generally, sulfuric acid of 93–99% is used. The sulfuric values may be fed to the plant as H_2SO_4, oleum (20% SO_3), or even SO_3 (see SULFURIC ACID AND SULFUR TRIOXIDE). Commonly, both H_2SO_4 and oleum are used. The split between the two is determined by water balance. All water entering the process or produced by side reactions reacts with the SO_3 component of the oleum:

$$H_2O + SO_3 \rightarrow H_2SO_4$$

The ratio of fluorspar to sulfuric acid fed depends on the relative cost of each raw material. As of this writing, fluorspar is more expensive than sulfuric acid; thus, most often a slight excess of sulfuric acid is desirable. Too much sulfuric acid, however, yields a reaction mixture which becomes wet, sticky, corrosive, and hard to handle.

3.2. Technology. The key piece of equipment in a hydrogen fluoride manufacturing plant is the reaction furnace. The reaction between calcium fluoride and sulfuric acid is endothermic (1400 kJ/kg of HF) (334.6 kcal/kg), and for good yields, must be carried out at a temperature in the range of 200°C. Most industrial furnaces are horizontal rotating kilns, externally heated by, for example, circulating combustion gas in a jacket. Other heat sources are possible, eg, supplying the sulfuric acid value as SO_3 and steam (qv), which then react and condense, forming sulfuric acid and releasing heat.

Even at the small production rates involved with the earliest HF production, the fundamental technical problem of HF production was apparent. When finely ground spar and acid are mixed in the proper proportions, a thin, almost watery slurry is obtained. Little reaction occurs until the suspension is heated. Upon heating, the slurry thickens rapidly, passing into a sticky paste that can build up on the furnace walls, thus reducing heat transfer. Additionally, intimate mixing of spar and acid is required, and paste formation interferes with this. The fundamental problem in designing an HF furnace is thus to find a method to keep the heat-transfer surfaces clean enough to allow the reaction to proceed at a reasonable rate, and to keep the reaction mass from forming a sticky material.

Historically, internal scrapers or paddles were used in some designs, and loose rails were used in others to break up any caking material which formed. The nature of these designs mechanically limited the furnaces to relatively small sizes producing about 3000 t/yr. High maintenance costs were also involved.

In the 1960s the need for improved technology extendable to higher capacities became apparent, and several new approaches were commercialized. One example is the use of a heavy-duty mechanical mixer to partially react the spar and acid. This first reaction phase carries the reaction past the point where sticky material forms, enabling the reaction to be completed on a flowable solid material in a standard externally jacketed rotating kiln. A second technology employs an Archimedean screw fixed to the rotating shell, to bring sufficient quantities of hot, dry solid from the discharge end of the furnace to the feed end, such that any sticky material formed is absorbed by the dry solid. This method also serves to bring the reactants up to reaction temperature quickly, by contact with the hot recycled material (35). In both of these technologies, large ($<$10,000 t/yr) furnace capacities are attainable, and the furnaces can be made largely from inexpensive carbon steel.

In all HF processes, the HF leaves the furnace as a gas, contaminated with small amounts of impurities such as water, sulfuric acid, SO_2, or SiF_4. Various manufacturers utilize different gas handling operations, which generally include scrubbing and cooling. Crude HF is condensed with refrigerant, and is further purified by distillation (qv). Plant vent gases are scrubbed with the incoming sulfuric acid stream to remove the bulk of the HF. The sulfuric acid is then fed to the furnace. Water or alkali scrubbers remove the remainder of the HF from the plant vent stream.

Some manufacturers recover by-products from the process. Fluosilicic acid [16961-83-4], which is used in water fluoridation, can easily be recovered from the plant vent gases, which contain SiF_4:

$$SiF_4 + 2\,HF \rightarrow H_2SiF_6(aq)$$

The calcium sulfate [7778-18-9] discharged from the furnace can also be recovered. This is less the practice in the United States where natural gypsum is plentiful and inexpensive than in Europe, where $CaSO_4$ recovery for use in cement (qv) and self-leveling floors is common. Some $CaSO_4$ is recovered in the United States, primarily for lower end uses such as road aggregate.

Figure (10) is a schematic of a typical HF process.

A process for preparing hydrogen fluoride in a uniformly high conversion at a high space-time yield with minimal energy consumption by reaction of fluorspar and sulfuric acid in a rotary tube furnace has been described (36).

3.3. Alternative Processes. Because of the large quantity of phosphate rock reserves available worldwide, recovery of the fluoride values from this raw material source has frequently been studied. Strategies involve recovering the fluoride from wet-process phosphoric acid plants as fluosilicic acid [16961-83-4], H_2SiF_6, and then processing this acid to form hydrogen fluoride.

Numerous processes have been proposed, but none has been commercialized on a large scale (37). The overall reaction in such processes is

$$H_2SiF_6 + 2\,H_2O \rightarrow 6\,HF + SiO_2$$

However, this reaction does not take place in a single step, and multiple reactions must be used. One such route involves using sulfuric acid to decompose the H_2SiF_6:

$$H_2SiF_6 \xrightarrow{H_2SO_4} 2\,HF + SiF_4$$

followed by hydrolysis of the SiF_4 in either the vapor or liquid phases:

$$3\,SiF_4(l) + 2\,H_2O \rightarrow 2\,H_2SiF_6 + SiO_2$$
$$SiF_4(g) + 2\,H_2O \rightarrow > 600^{\circ}C\ 4\,HF + SiO_2$$

Other technologies proceeding via intermediates such as NH_4F or KHF_2 are also possible. A more recently developed process (37) involves the reaction of the H_2SiF_6 and phosphate rock, producing a calcium silicon hexafluoride ($CaSiF_6$) intermediate that can be converted to CaF_2 and then to HF by reaction of H_2SO_4. All of the processes produce silica. The quality of the silica varies greatly, and its value as a coproduct has a significant impact on the processes' economics.

The future for these technologies is uncertain. Economic comparisons with fluorspar-based processes indicate that as long as fluorspar supplies remain abundant, there is little justification to proceed with such processes.

3.4. Materials of Construction. Acceptable materials of construction for hydrogen fluoride handling are a function of such variables as temperature, hydrogen fluoride strength, and method of use. As examples of the latter, corrosion is greater for higher velocities as well as for metals used in reboiler heat-transfer surfaces. Mild steel is generally used for most anhydrous hydrogen fluoride applications, up to 66°C. Steel, in contact with HF, forms a passive film of iron fluoride, which then protects the metal against further corrosion. Any physical or chemical action which disrupts this passive film can lead to substantial increases in corrosion rate. In steel service, hydrogen blistering, caused by accumulation of hydrogen released by corrosion at laminations and inclusions in the steel, may occur and must be evaluated during periodic inspections.

At higher temperatures, Monel, a nickel–copper alloy, is suitable, as is Hastelloy-C, a nickel molybdenum–chromium alloy.

Aqueous hydrogen fluoride of greater than 60% may be handled in steel up to 38°C, provided velocities are kept low (>0.3 m/s) and iron pickup in the process stream is acceptable. Otherwise, rubber or polytetrafluoroethylene (PTFE) linings are used. For all applications, PTFE or PTFE-lined materials are suitable up to the maximum use temperature of 200°C. PTFE is also the material of choice for gasketing. Alloy 20 or Monel is typically used for valve and pump applications. Materials unacceptable for use in HF include cast iron, type 400 stainless steel, hardened steels, titanium, glass, and silicate ceramics.

4. Economic Aspects

4.1. Production. Table 4 summarizes North American capacity for hydrogen fluoride. Production is by the reaction of acid-grade fluorspar with sulfuric acid (38). Demand for 2001 was 350×10^3 t. Projected demand for 2005 is 364×10^3t. Demand will be impacted by the phase out of HCFC-141b refrigerant in January 2003.

HF imports decreased nearly 15% in 2001 as compared with 2000 (39). U. S. imports of HF by country are listed in Table 5.

Current price for HF is $0.29/kg ($0.65/lb) list aqueous 70% bulk (38).

4.2. Fluorspar Supply. Production costs of hydrogen fluoride are heavily dependent on raw materials, particularly fluorspar, and significant changes have occurred in this area. Identified world fluorspar resources amount to approximately 500×10^6 metric tons of fluorspar (40). Table 6 lists world mine production, reserves, and reserve base (40).

Fluorspar is marketed in three grades: acid, ceramic, and metallurgical. Metallurgical grade is commonly sold as lump or gravel, and ceramic-grade as a dried flotation filter cake or as briquettes or pellets. Acid-grade is used for HF manufacture and is the uprest form, having a minimum CaF_2 content of 97%. Most of the acid-grade spar used for HF production in the United States is imported. Most acid-grade imports come from China and Africa. In the United States about 80% of reported fluorspar consumption went into the production of hydrofluoric acid (HF) in Louisiana and Texas and aluminum fluoride in Texas. HF is the primary feedstock for the manufacture of virtually all organic and inorganic fluorine-bearing chemicals, and is also a key ingredient in the processing of aluminum steelmaking, in iron and steel foundries, primary aluminum production, glass manufacture, enamels, welding rod coatings, cement production, and other uses or products (40).

Purity is expected to become a significant concern as reserves are depleted. Higher levels of impurities in the fluorspar may require modifications to HF production technology to produce high quality hydrogen fluoride. This happened regarding high arsenic levels in some Mexican fluorspar. Both Fluorex and Allied-Signal have installed facilities to remove arsenic from the HF proces. In addition, the Kenyan fluorspar production contains high levels of phosphate impurity which had to dealt with.

5. Specifications, Shipping, and Analysis

Hydrogen fluoride is shipped in bulk in tank cars (specification 112S400W) and tank trucks (specification MC312). A small volume of overseas business is shipped in ISO tanks. Bulk shipments are made of anhydrous HF as well as 70% aqueous solutions. A small amount of aqueous solution may be shipped as 50%. Cars and trucks used for anhydrous HF transport are of carbon steel construction. It is possible to ship 70% aqueous in steel from a corrosion standpoint; however, rubber lining is commonly used to eliminate iron pickup, which is detrimental to product quality in a number of applications. Hydrogen fluoride of less than 60% strength must always be shipped in lined containers.

An improved method for safe storage, transporation, and handling of hydrogen fluoride has been described in a patent application (41). It involves lowering the vapor pressure of HF using a sulfone diluent.

Anhydrous hydrogen fluoride is also available in cylinders, and aqueous hydrogen fluoride, either 50% or 70%, is also shipped in polyethylene bottles and carboys. Typical product specifications and analysis methods are given in Table 7.

6. Environmental Concerns

Although it is widely recognized as a hazardous substance, large volumes of HF are safely manufactured, shipped, and used, and have been for many years. Excellent manuals describing equipment and procedures for the safe handling of hydrogen fluoride are available from manufacturers (16,17,43).

The hydrogen fluoride industry has undertaken a significant effort to investigate the behavior of HF releases so as better to define the risks associated with an accidental spill, and to design effective mitigation systems. A series of tests conducted in the Nevada desert in 1986 showed that spills of pressurized, super-heated HF under certain conditions could form a heavier-than-air vapor cloud consisting of flashed, cold HF vapor and an entrained aerosol of HF droplets. The HF did not form liquid pools as expected, reducing the effectiveness of diking in mitigating the effect of a release (44). The effect of water sprays in mitigating an HF release was studied in detail as one of several components of the Industry Cooperative Hydrogen Fluoride Mitigation and Ambient Impact Assessment Program (ICHMAP). Water spray curtains or water monitors were found to remove between 25 and 95% of HF released in field tests. The removal efficiency depended primarily on the ratio of water to HF volume. The higher removal efficiency was obtained at a 50:1 ratio with a single spray curtain (45).

7. Health and Safety Aspects

Mild exposure to HF via inhalation can irritate the nose, throat, and respiratory system. The onset of symptoms may be delayed for several hours. Severe exposure via inhalation can cause nose and throat burns, lung inflammation, and pulmonary edema, and can also result in other systemic effects including hypocalcemia (depletion of body calcium levels), which if not promptly treated can be fatal. Permissible air concentrations are (43,46) OSHA PEL, 3 ppm (2.0 mg/m^3) as F; OSHA STEL, 6 ppm (5.2 mg/m^3) as F; and ACGIH TLV, 3 ppm (2.6 mg/m^3) as F. Ingestion can cause severe mouth, throat, and stomach burns, and may be fatal. Hypocalcemia is possible even if exposure consists of small amounts or dilute solutions of HF.

Both liquid HF and the vapor can cause severe skin burns which may not be immediately painful or visible. HF can penetrate skin and attack underlying tissues, and large (over 160 cm^2) burns may cause hypocalcemia and other systemic effects which may be fatal. Even very dilute solutions may cause burns. Both liquid and vapor can cause irritation to the eyes, corneal burns, and conjunctivitis.

Unlike other acid burns, HF burns always require specialized medical care. The fluoride ion is extremely mobile and easily penetrates deeply into the skin. Immediate first aid consists of flushing the affected area with copious quantities of water for at least 20 minutes. Subsequently the area is immersed in iced 0.13% benzalkonium chloride solutions or massaged with 2.5% calcium gluconate gel. For larger burns, subcutaneous injection of 5% calcium gluconate solution beneath the affected area may be required. Eye exposure requires flushing with water for at least 15 minutes, and subsequent treatment by an eye specialist. Exposure to HF vapor should be treated by moving the victim to fresh air, followed by artificial respiration if required, and administration of oxygen if the victim is having difficulty breathing. As in other cases of exposure, a qualified physician must be called, and the victim should be held under observation for at least 24 hours. First aid for swallowed HF consists of drinking large quantities of water; milk or several ounces of milk of magnesia may be given. Vomiting should not be induced.

Hydrogen fluoride is not a carcinogen. However, HF is highly reactive, and heat or toxic fumes may be evolved. Reaction with certain metals may generate flammable and potentially explosive hydrogen gas.

Many opportunities for dermal and inhalation exist in the high technology industries. Numerous reports of injuries and due to HF have occurred (47).

8. Uses

In the North American HF market, approximately 57% goes into the production of fluorocarbons, 3% to the nuclear industry, 3% to alkylation processes, 3% to steel pickling, and 20% to other markets (38). This does not include the HF going to aluminum fluoride, the majority of which is produced captively for this purpose.

8.1. Fluorocarbons.

Fluorocarbons are a family of products that have properties which render them valuable as refrigerants, blowing agents, solvents, and sources of raw materials for production of fluoropolymer materials. Other specialty fluorine-containing, organic chemicals are also produced, some of which are used as anesthetics and fire extinguishants. Certain chlorofluorocarbon products are thought to be damaging to the ozone layer of the upper atmosphere and this market is changing to nonozone-damaging fluorocarbon products. The ban on HCFC 1416 production and importation goes into effect January 1, 2003.

HF is used as a source of fluorine for production of all the various fluorocarbon products. HF reacts in the presence of a suitable catalyst and under the appropriate temperature and pressure conditions with various organic chemicals to yield a family of products. A by-product stream of hydrochloric acid may be coproduced.

Projection of HF requirements for this market segment is uncertain. The ultimate volume of this market segment is negatively impacted by replacement of fluorocarbons with nonfluorine-containing products for foam blowing and solvents. Sales of fluorocarbons would also be reduced by conservation, recovery, and recycle encouraged by high fluid cost, taxation, or regulation. The production of high growth fluorine-containing plastics would be unaffected.

It appears that the ultimate replacements for the high volume chlorofluorocarbon products are to be more highly fluorinated organic chemicals, thus requiring significantly higher volumes of HF in their manufacture. The HFC replacements have no ozone-depletion potential because they contain no chlorine (39).

8.2. Nuclear Industry.

Technology in the manufacture of uranium reactor fuel for commercial electric power generation requires the uranium to be converted to gaseous uranium hexafluoride [7783-81-5], UF_6, so that enrichment may occur. UF_6, the only gaseous form of uranium, is the form used for the enrichment processes (see DIFFUSION SEPARATION METHODS). Following enrichment, reactor fuel elements are manufactured by converting to UO_2. Domestic U.S. nuclear power generation is not expected to grow. Most of the future demands for UF_6 are expected to be dictated by development of overseas reactor installations. Some other nuclear markets employing UF_6 involve weapons systems but usage and future growth is expected to be low.

To convert naturally occurring uranium oxide, yellow cake or U_3O_8, to the gaseous UF_6, hydrofluoric acid is first used to convert the U_3O_8 to UF_4. Further fluorination using fluorine (generated from more HF) is employed to convert the UF_4 to UF_6. The UF_6 is then processed at gaseous diffusion enrichment plants.

8.3. Alkylation. Petroleum and, to a lesser extent, detergent aklylation are processes which make use of the particular catalytic properties of anhydrous HF. Petroleum alkylation produces a very high octane gasoline blending component (C-7 or C-8 compounds) by condensation of C-3 or C-4 olefins obtained in the catalytic cracking process along with isobutane. Detergent alkylation generates a desirable biodegradable detergent intermediate. Although HF is used as a catalyst in these processes, the HF is slowly consumed because of side reactions, with impurities contained in the various feeds and feed additives, nonruminant feeds (qv).

In the petroleum alkylation process, liquid anhydrous HF is intimately contacted with isobutane [75-28-5] and mixed light olefins under pressure at an elevated (about 40°C) temperature to produce a branched-chain fuel having very high octane value. The mixture of HF and hydrocarbon is settled, the acid is recycled, and the alkylate is water-washed and dried. The HF catalyzes a broad range of desirable reactions in this process and although some HF is lost through reaction with impurities in the various feedstocks, regeneration of most of the HF is easily accomplished within the alkylation unit. The drawoff from this acid regeneration system is neutralized before disposal. This equates to the HF consumption of this process.

Increasing demand for higher octane, lead-free motor fuel having low volatility makes the alkylation process a proven way to maximize profitability. Alkylation using sulfuric acid as the catalyst competes with the HF process even though acid consumption and regeneration costs are much greater.

The choice between sulfuric and hydrofluoric acid-catalyzed processes for new alkylation capacity is influenced by proximity to sulfuric acid regeneration plants, energy costs, and the nature of the unit feed. HF produces a higher quality alkylate when the unit feed is rich in propenes or isobutene. Sulfuric acid is preferred when the feed is rich in pentenes or *n*-butene. Additionally, in some quarters the perception exists that the sulfuric acid alkylation process may be less hazardous and may present a lesser potential environmental threat. As a result, future installation of additional grass roots HF alkylation units in North America may be affected. Industry is working toward development of chemical additives which, when combined with HF, reduce the risks associated with an accidental release. The success of such work could have a significant impact on the alkylation market. However, hydrofluoric acid used for petroleum alkylation has been strong because of high refinery operating rates (38).

8.4. Chemicals. Both organic and inorganic fluorine-containing compounds, most of which have highly specialized and valuable properties, are produced from HF. Typically these fluorinated chemicals are relatively complex, sometimes difficult to manufacture, and of high value. These materials include products used as fabric and fiber treatments, herbicide and pharmaceutical intermediates, fluoroelastomers, and fluorinated inert liquids. Other products include BF_3, SF_6, and fluoborates.

Many different processes using HF as a reactant or source of fluorine are employed in the manufacture of fluorinated chemical derivatives. In many cases the chemistry employed is complex and in some cases proprietary. Electrochemical fluorination techniques and gaseous fluorine derived from HF are used in some of these applications.

Some of the chemical derivatives, especially those tied to agricultural uses, tend to experience some cyclical demand. However, because of the specialized nature of many of the fluorinated chemicals, these products are positioned in strong, high performance market areas having above average growth rates.

8.5. Aqueous HF.

Aqueous solutions of hydrofluoric acid are used in stainless steel pickling (see METAL TREATMENTS), chemical milling, glass (qv) etching, exotic metals extraction, quartz purification, and a variety of other uses including metal coatings (qv) and other, small-volume, upgraded inorganic fluorine compounds. A substantial portion of aqueous HF is marketed through distributors as drummed or packaged product.

A small but significant use for aqueous HF is in the electronics industry (see ELECTRONIC MATERIALS). Aqueous HF (typically 49%) of extremely high purity is used as an etchant for silicon wafers.

8.6. Aluminum Industry.

Large amounts of HF are consumed in the production of aluminum fluoride [7784-18-1], AlF_3, and cryolite [15096-52-3] (sodium aluminum fluoride), used by the aluminum industry. Both of these compounds are used in the fused alumina bath from which aluminum is produced by the electrolytic method.

Most AlF_3 and cryolite producers have their own HF production facilities. HF vapor is reacted with alumina trihydrate to form AlF_3 in a fluid-bed reactor. HF is reacted with sodium hydroxide to form sodium fluoride, which is then used to produce cryolite. Producers who manufacture these products solely for use in the aluminum industry do not generally install liquid HF storage and handling facilities, and do not participate in the merchant HF market.

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Table 1. **Properties of Anhydrous Hydrogen Fluoride**

Property	Value	Reference
formula weight	20.006	
composition, wt%		
H	5.038	
F	94.96	
boiling point at 101.3 kPa, °C	19.54	1
critical pressure, MPa	6.48	2
critical temperature, °C	188.0	2
critical density, g/mL	0.29	2
critical compressibility factor	0.117	2
melting point, °C	−83.55	3
density, liquid, 25°C, g/mL	0.958	4
heat of vaporization, 101.3 kPa, kJ/mol	7.493	1
heat of fusion, −83.6°C, kJ/mol	3.931	5
heat capacity, constant pressure, liquid at 16°C, J/(mol · K)	50.6	5
heat of formation, ideal gas, 25°C, kJ/mol	−272.5	6
free energy of formation, ideal gas, 25°C, kJ/mol	−274.6	6
entropy, ideal gas, 25°C, J/(mol · K)	173.7	6
vapor pressure, 25°C, MPa	122.9	7
viscosity, liquid, 0°C, mPa · s (=cP)	0.256	8
surface tension, mN/m (=dyne/cm), 0°C	10.2	9
refractive index, liquid, 25°C, 589.3 nm	1.1574	10
molar refractivity, cm^3	2.13	10
dielectric constant, at 0°C	83.6	11
dipole moment, C · m	6.104×10^{-30}	12
thermal conductivity, at 25°C, J(s · cm · °C)		
liquid	4.1×10^{-3}	13
vapor	2.1×10^{-4}	13
cryoscopic constant, K_f, mol/(kg · °C)	1.52	3
ebullioscopic constant, K_b, mol/(kg · °C)	1.9	14

[a] To convert kPa to psi, multiply by 0.145.

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

[c] To convert C · m to debye, divide by 3.336×10^{-30}.

Table 2. **Properties of 70% Aqueous Hydrogen Fluoride**

Property	Value	Reference
boiling point at 101.3 kPa, °C	66.4	19
freezing point, °C	−69	20
density, 0°C, g/mL	1.258	21
vapor pressure, 25°C, kPa	20	22
viscosity, 25°C, mPa · s (=cP)	0.61	23
specific heat, 25°C, J/(g · °C)	0.675	23

[a] To convert kPa to psi, multiply by 0.145.

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

Table 3. **Solubility of Metal Fluorides in Anhydrous Hydrogen Fluoride**[a]

Fluoride	Temperature, °C	Solubility, g/100 g
LiF	12	10.3
NaF	11	30.1
KF	8	36.5
NH_4F	17	32.6
CaF_2	12	0.817
SrF_2	12	14.83
BaF_2	12	5.6
MgF_2	12	0.025
FeF_2	12	0.006
FeF_3	12	0.008
AlF_3	11	<0.002
SbF_5	25	miscible

[a] Ref. 8.

Table 4. **North American Capacity of Hydrofluoric Acid**[a]

Producer	Capacity × 10^3 t
Alcan Aluminum, Jonquiere, Quebec, Canada	34
DuPont, La Porte, Tex.	80
Honeywell, Geismar, La.	130
Honeywell, Amherstburg, Ontario, Canada	52
Industrias, Quimicas, San Luis Potosi, Mexico	7
Quimbasicos, Monterrey, Mexico	6
Quimica Fluor, Matamoros, Mexico	94
Solvay Fluor Mexico, Juarez, Mexico	31
Total	*434*

[a] Ref. 38.

Table 5. **U.S. Imports For Consumption of Hydrofluoric Acid, by Country**[a, b]

	2000		2001	
Country	Quantity, t	Value × 10^3\$	Quantity, t	Value × 10^3\$
Canada	36,000	41,100	26,300	31,000
China	144	99	114	84
France	212	209	111	108
Germany	150	285	342	543
India	0	0	14	4
Ireland	0	0	211	212
Japan	1,670	4,590	1,130	2,930
Korea, Republic of	80	329	63	248
Mexico	92,400	84,500	83,000	78,300
United Kingdom	163	189	147	146
Total	*131,000*	*131,000*	*112,000*	*114,000*

[a] Ref. 39.

[b] Data are rounded to no more than three significant digits; may not add to totals shown.

[c] Cost, insurance, freight values at U.S. ports.

Table 6. **World Mine Production, Reserves, and Reserve Base of Fluorspar**[a]

	Mine Production			
	2000	2001[b]	Reserves[c]	Reserve base[d]
United States	NA	NA	NA	6,000
China	2,450	2,450	23,000	94,000
France	100	100	10,000	14,000
Italy	65	70	6,000	7,000
Kenya	90	100	2,000	3,000
Mexico	635	620	32,000	40,000
Mongolia	199	180	10,000	NA
Morocco	100	80	NA	NA
Namibia	66	83	3,000	5,000
Russia	160	160	moderate	18,000
South Africa	212	240	41,000	80,000
Spain	133	120	6,000	8,000
other countries	310	310	100,000	170,000
World total (may be rounded)	*4,520*	*4,510*	*230,000*	*440,000*

[a] Ref. 40.
[b] Estimated, NA = not available.
[c] Measured as 100% calcium fluoride.
[d] Data in wet tons.

Table 7. **Hydrogen Fluoride Product Specifications**[a]

Component	Specification[b]	Analytical method
	Anhydrous HF	
HF, wt%	99.95[c]	difference
nonvolatile acid, ppm	100	evaporation/titration
sulfur dioxide, ppm	50	iodimetry
water, ppm	200	conductivity
arsenic, ppm	25	colorimetry
fluosilicic acid, ppm	100	colorimetry
	Aqueous HF	
HF, wt%	70–72	titration
nonvolatile acid, ppm	200	evaporation/titration
sulfur dioxide, ppm	100	iodimetry
arsenic, ppm	18	colorimetry
fluosilicic acid, ppm	100	colorimetry

[a] Ref. 42.
[b] Values are the maximum allowable unless otherwise stated.
[c] Value is the minimum allowable.

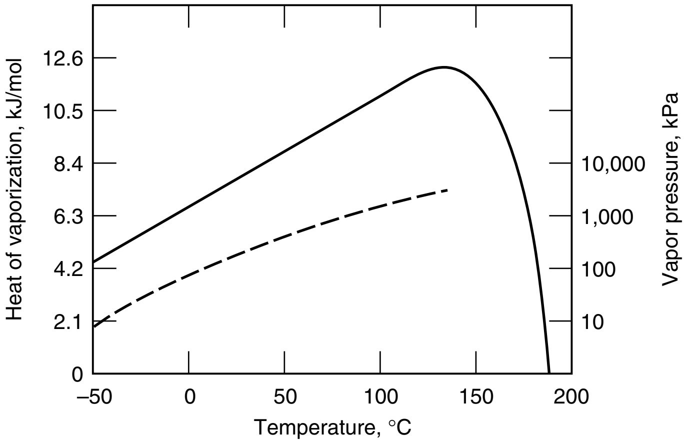

Fig. 1. (—) Latent heat of vaporization (1,7) and (- - -) vapor pressure (1,4,7,15) of anhydrous hydrogen fluoride. To convert kPa to psi, multiply by 0.145. To convert kJ to kcal, divide by 4.184.

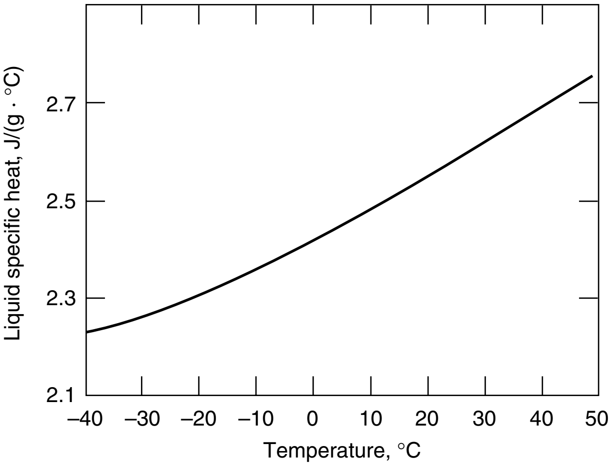

Fig. 2. Specific heat of liquid anhydrous hydrogen fluoride (5,16). To convert J to cal, divide by 4.184.

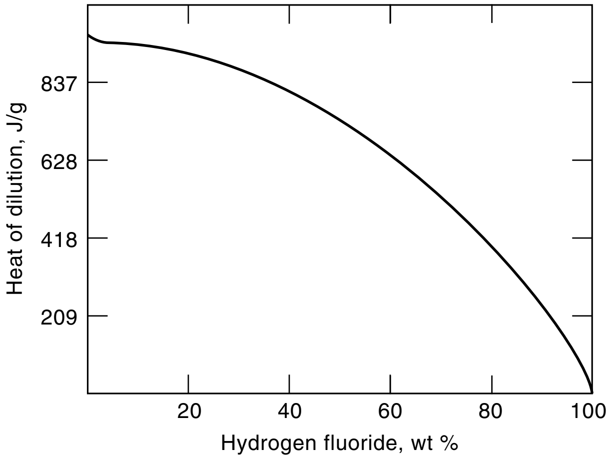

Fig. 3. Heat of solution per gram of anhydrous hydrogen fluoride in water when mixed to the final concentration shown in wt% of HF (16–18)

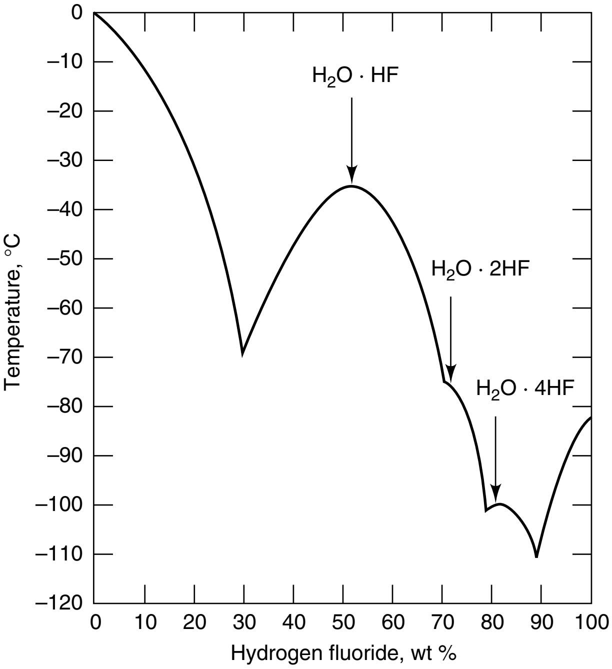

Fig. 4. Freezing point, HF−water system (24).

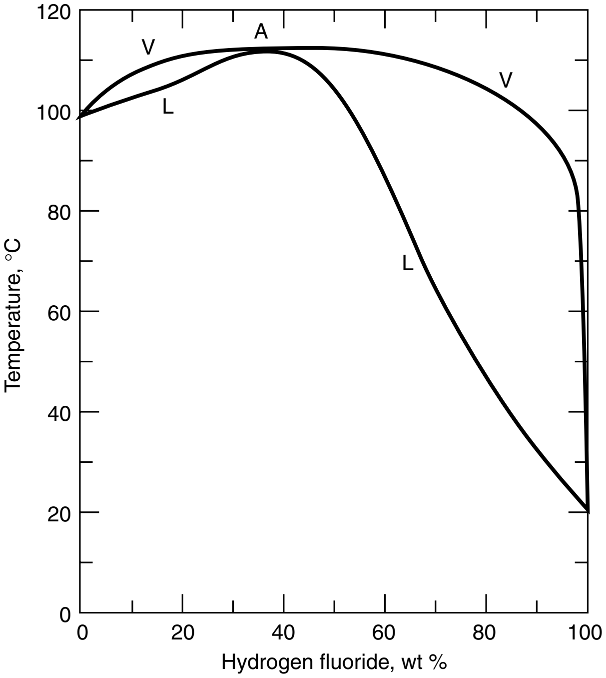

Fig. 5. Boiling point curve for the HF–water system, where A represents an azeotrope at 37.73 wt% HF, L is the liquid, and V the vapor (25,26).

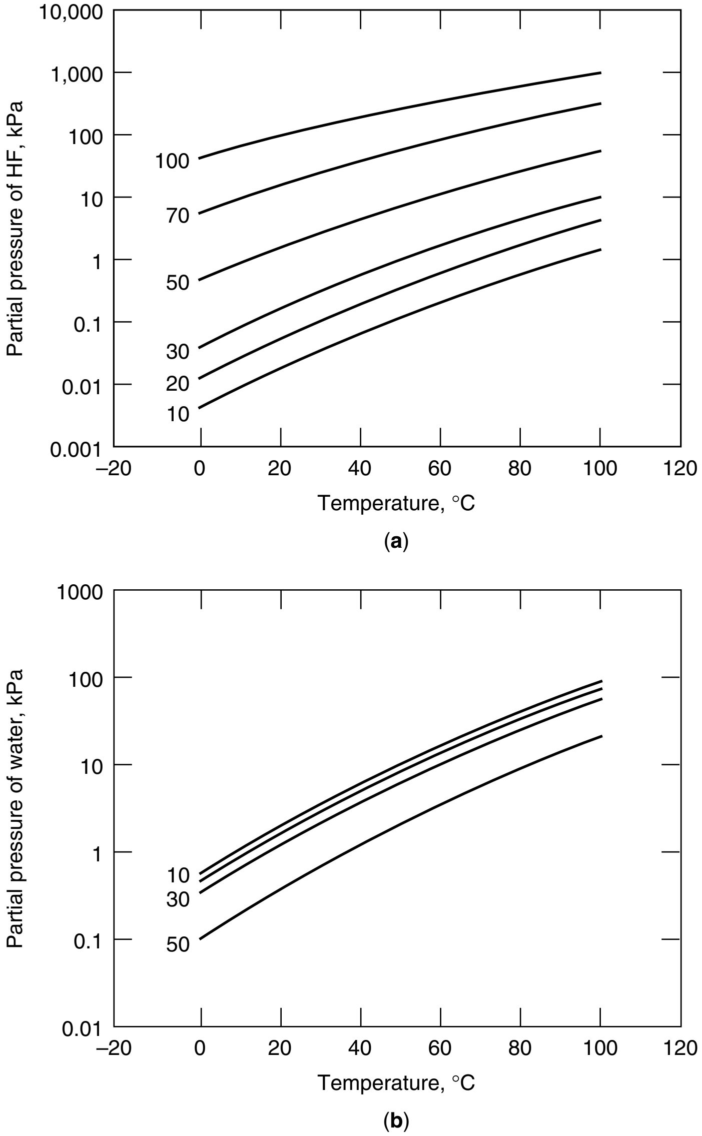

Fig. 6. Partial pressures over HF–water solutions where the numbers represent the quantity of HF in solution expressed as wt % (**a**) of HF and (**b**) of H_2O (22).

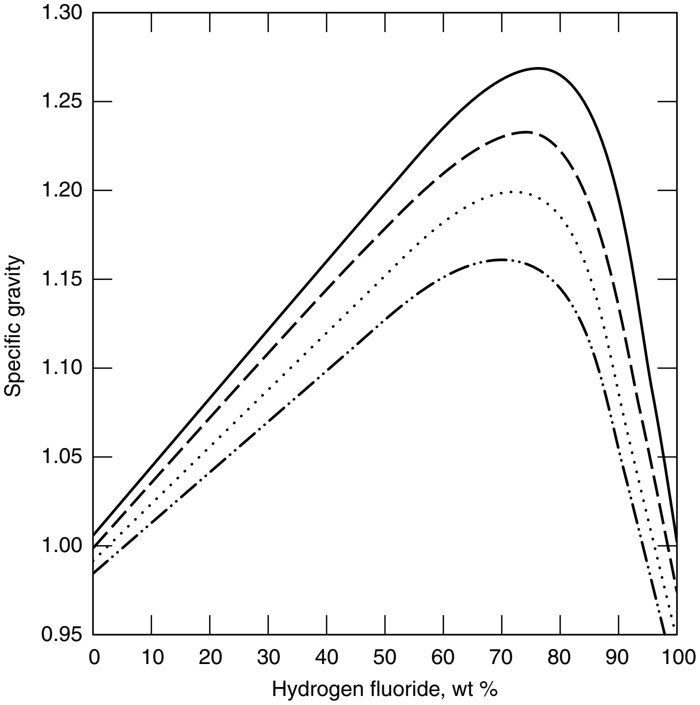

Fig. 7. Specific gravity of HF−water solutions where (–) represents 0°C, (—) 20°C, (····) 40°C, and (–··–··) 60°C (21–23).

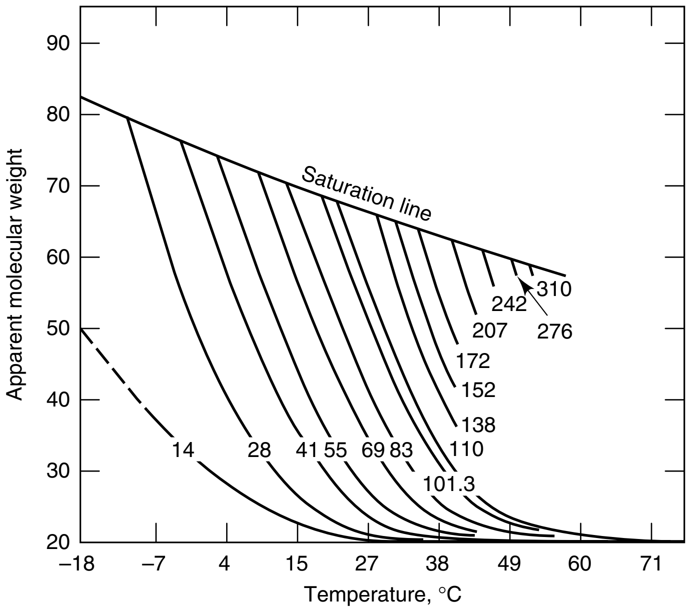

Fig. 8. Apparent vapor molecular weight of anhydrous HF where the numbers represent the partial pressure of HF in kPa. To convert kPa to psi, multiply by 0.145 (1,17,20,31,33).

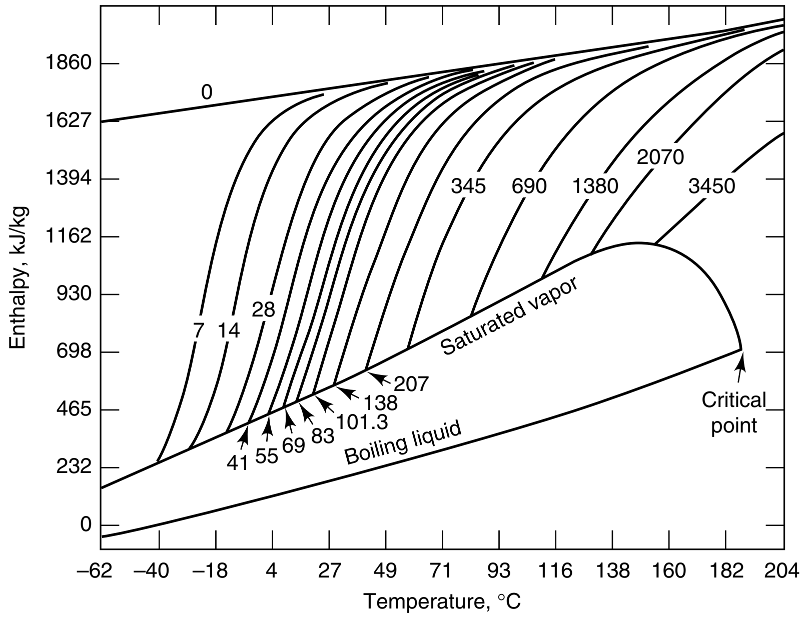

Fig. 9. Vapor-phase enthalpy of anhydrous HF where the numbers represent the partial pressure of HF in kPa (1,17,20,31,33). The critical point occurs at 188°C. To convert kPa to psi, multiply by 0.145. To convert kJ/kg to Btu/lb, multiply by 4.302×10^{-4}.

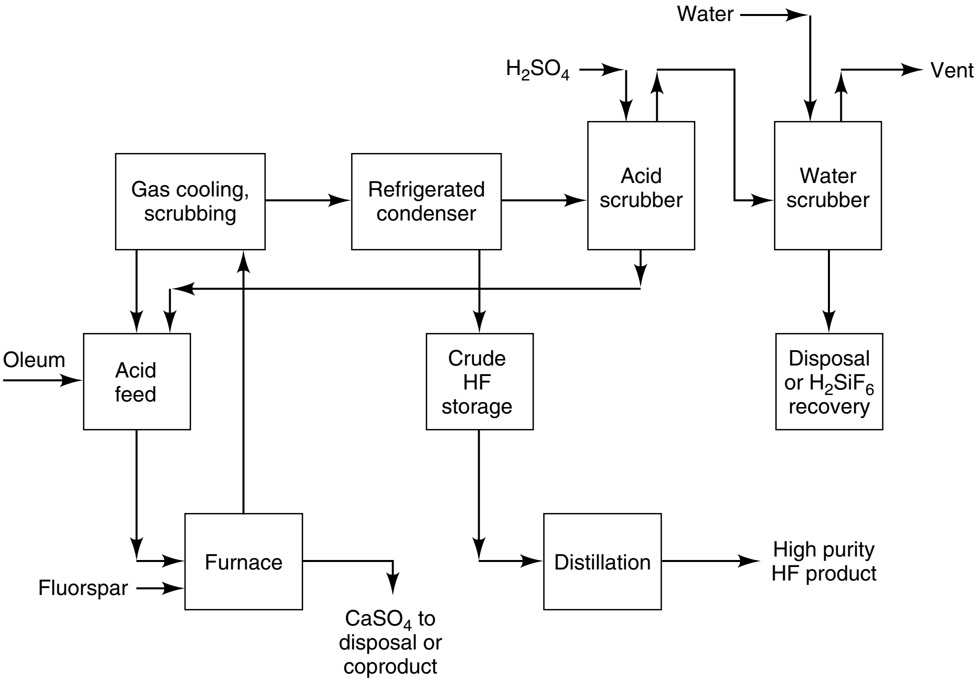

Fig. 10. Hydrogen fluoride manufacturing process.