HYDROFLUORIC ACID
AP-42 Section 5.8
Reference Number
2

KIRK+ OTHMER

HF acid

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HYDROGEN FLUORIDE. In volume of production, hydrogen fluoride (hydrofluoric acid, HF) is the most important manufactured compound of fluorine. Both the anhydrous and aqueous acids are used directly, and as intermediates in forming other fluorine-containing products.

Anhydrous hydrogen fluoride is a colorless liquid or gas (bp 19.5°C), highly water soluble and fuming strongly in contact with the atmosphere. The formula weight is 20.006, but hydrogen bonding between molecules produces extensive polymerization, and the liquid and gas show large departures from ideal behavior.

Hydrogen fluoride must have been made when Schwankhard of Nürnberg in 1670 etched glass with fluorspar. Marggraf in 1764 showed that the etchant was a gas; Scheele in 1771 showed that a new acid had been discovered; and Ampère in 1810 and Davy in 1813 and 1814 proved that the compound we now know as hydrogen fluoride contained a new element (1).

The classical, quite limited uses for hydrogen fluoride, such as glass etching and polishing, foundry scale removal, and minor production of metal fluorides, predominated until the 1930s. Through 1935–1940 the enormous increase in aluminum production brought an equivalent requirement for hydrogen fluoride, employed captively for making the aluminum fluoride and synthetic cryolite used in the electrochemical reduction of aluminum oxide.

Anhydrous hydrogen fluoride was first made by Frémy in 1856 (2), but there was no significant commercial preparation until 1931, when the first bulk shipment was made by Sterling Products Company (merged in 1939 with Pennsalt Chemicals Corporation). The impetus for this was the use of the anhydrous acid in making **chlorofluorohydrocarbons**, introduced as refrigerating fluids (Kinetic Chemicals Corp., a joint venture of Du Pont and Frigidaire Corp., 1930). Under the stimulus of wartime need, new major uses for anhydrous hydrogen fluoride developed, including alkylation catalysis to manufacture aviation gasoline (Phillips Petroleum Company, 1942); use of chlorofluorohydrocarbons for pressurized packaging (U.S. Dept. of Agriculture, 1942); and the manufacture of uranium fluorides (Manhattan District Engineers, 1942). The growth of all of these industries and the addition of requirements for stainless-steel pickling and fluorine-containing plastics brought the volume of hydrogen fluoride production to the current high and still rising levels.

Table 1. The Physical Properties of Anhydrous Hydrogen Fluoride

		References
formula weight (calculated)	20.006	
molecular weight		
saturated vapor, at boiling point	78.24	6
saturated vapor, at 100°C	49.08	6
boiling point, at 1 atm	19.51°C	6
melting point	−83.37°C	7
density		
liquid, at 25°C	0.9576 g/cm³	8
vapor, saturated, at 25°C	3.553 g/liter	6
vapor pressure, at 25°C	17.8 psia	6
heat of vaporization		
boiling point, at 1 atm	1609 cal/20.01 g	6[a]
	1785	9[b]
heat of fusion, melting point	46.93 cal/g	7
heat capacity, constant pressure		
liquid, boiling point	12.2 cal/(20.01 g) (°C)	7
vapor, at 25°C, 1 atm	143 cal/(20.01 g) (°C)	10
heat of formation		
ideal gas, at 25°C[c]	−64.9 kcal/20.01 g	12
free energy of formation		
ideal gas, at 25°C[c]	−65.0 kcal/20.01 g	13
entropy, ideal gas, at 25°C[c]	41.5 cal/(20.01 g)(°C)	13
critical temperature	188°C	8
critical pressure	941 psia	8
critical density	0.29 g/cm³	8
viscosity, at 0°C	0.26 cP	14
surface tension, at boiling point	8.6 dyn/cm	15
refractive index, 5893 Å, at 25°C	1.1574	16
molar refractivity (5893 Å, formula wt)	2.13 cm³	16
conductivity, at 0°C	$<1.6 \times 10^{-6}$ mho/cm	17
dielectric constant, at 0°C	83.6	18
dipole moment, HF molecule	1.83 D	19

[a] From vapor pressure vs temperature.

[b] From calorimetry.

[c] The enthalpy change for the reaction HF (ideal gas) → HF (real gas), at 25°C, 1 atm, is uncertain, and may exceed several kilocalories per mole (20).

Manufacture

The preferred raw materials for the manufacture of hydrogen fluoride in the United States are acid-grade fluorspar (see Calcium fluoride, p. 573) and sulfuric acid:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2\ HF$$

The ability of the reaction to proceed to the maximum degree in commercial operation is influenced by the purity and fineness of the fluorspar, the concentration of the sulfuric acid used, the ratio of sulfuric acid to fluorspar, the temperature of the reaction, the time allowed for completion of the reaction, and the intimacy of mixing of the acid and spar.

Since fluorine values dominate raw material costs, these factors are optimized to give maximum yield of hydrogen fluoride.

Acid-grade fluorspar is a finely ground flotation product having the following typical specifications:

Screen analysis: 1% on 100 mesh, 12% on 200 mesh, 30% on 250 mesh, 45% through 325 mesh

CaF_2	minimum 97.5–98%
SiO_2	maximum 1.0%
S	maximum 0.05%
H_2O	maximum 0.1%
$CaCO_3$	principal remainder

Silica is a highly objectionable contaminant, since each pound consumes 2.6 lb of fluorspar and 3.3 lb of sulfuric acid by the reaction:

$$SiO_2 + 2\ CaF_2 + 2\ H_2SO_4 \rightarrow SiF_4 + 2\ CaSO_4 + 2\ H_2O$$

When hydrogen fluoride containing SiF_4 is absorbed in water, a further loss of fluorine values occurs by the reaction:

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

Carbonates are harmful in consuming sulfuric acid, in producing foaming in the generator, and in contributing carbon dioxide to the gas stream where it acts as a noncondensible diluent to the hydrogen fluoride. Sulfur-bearing minerals in fluorspar (eg, galena, pyrites), may generate hydrogen sulfide or sulfur dioxide, contaminating the hydrogen fluoride, and sometimes causing deposits of sulfur in the gas-handling equipment.

In general, with other conditions constant, the finer the fluorspar the readier is the liberation of fluorine values from the spar and, thus, the better are the yields. Fluorspar of the screen size indicated above has been commercially utilized directly in the hydrogen fluoride kilns with good yields. However, it has been the practice of some manufacturers to grind this material further. Such additional grinding is an expensive operation involving some small handling loss of fluorspar, and a decision to employ this procedure must be based upon an economic evaluation of the improved yields as compared with other means of securing the same results.

Sulfuric acid with a concentration as low as 93% or as high as 99% has been reported to have been used in hydrogen fluoride manufacture. The more dilute the acid (in this range), the more fluid is the reacting mass during initial mixing, and the greater is the ease with which the liberation of the fluorine from the fluorspar takes place. Two important factors offset this: (1) The more dilute sulfuric acid is much more corrosive to the hydrogen fluoride generator, and (2) the greater amount of water present will leave the generator with the hydrogen fluoride gas and may be undesirable. Thus, modern practice has established 96% sulfuric acid as the minimum desirable acid strength. The use of sulfuric acid stronger than 98% will reduce the amount of water introduced into the generator and may be less corrosive to the materials of construction; however, the vapor pressure of sulfuric acid, which increases rapidly with concentration above 98%, will be such that excessive amounts of sulfuric acid will leave the generator with the hydrogen fluoride gas, thereby not only reducing the quantity available for reaction with spar but also contaminating all or part, depending on the recovery system, of the hydrogen fluoride produced. In addition, the formation of fluorosulfuric acid, FSO_3H, which also has an appreciable vapor pressure, will be increased and thus tend to deplete the reacting mass of sulfuric acid and contaminate the product.

The ratio of sulfuric acid to fluorspar charged to the hydrogen fluoride generator is seldom the exact stoichiometric ratio, since, depending upon the relative cost of fluorspar and sulfuric acid, one or the other is used in slight excess. In U.S. practice, economic operation demands the maximum release of fluorine from fluorspar and justifies the use of a 5–10% excess of sulfuric acid. It should be recognized, however, that too great an excess of sulfuric acid will result in a "wet" residue calcium sulfate, which will tend to be strongly fuming unless the sulfuric acid is driven out of the generator with the hydrogen fluoride by high generator temperatures.

The reaction of calcium fluoride and sulfuric acid is endothermic, and thus heat must be supplied to complete the reaction in a reasonable period of time. To effect a release of over 98% of the fluorine in the fluorspar, the reaction time is normally 30–60 min at 200–250°C with the hydrogen fluoride leaving the generator at 100–150°C. Obviously, the lowest operating temperatures at which good yields are obtainable are desirable to minimize corrosion of the generator.

200×9/5+32
360+32 = 392

250×9/5
450+32 = 482

In modern practice, hydrogen fluoride generators may be horizontal, externally fired rotary kilns, with spar fed continuously at the forward end by a screw conveyor. Acid is also added at the forward end of the kiln, and calcium sulfate residue is removed through an air lock at the opposite end.

Stationary reactors are also used, comprising of a long horizontal vessel of U-shaped cross section containing a central shaft extending the full length, the shaft being equipped with mixing and conveying paddles. As in the rotary kiln, spar and acid move concurrently down the length of the reactor.

Sometimes a combination is used, in which a stationary premixer receives spar and heated sulfuric acid and feeds the well-mixed but incompletely reacted components into a heated rotary kiln.

Since hydrogen fluoride is readily absorbed by water, early manufacturers made an aqueous solution of the gases from the generator and prepared strong acids by fractionation, or by distillation with sulfuric acid when strengths above the atmospheric pressure azeotrope (38%) were needed.

Current requirements are principally for the anhydrous acid, so that manufacturers for merchant sale have succeeded in controlling conditions in the generator to supply effluent gas low enough in water and noncondensibles to permit direct condensation with reboiling to give anhydrous hydrogen fluoride directly. Vent gases must still be scrubbed with water to recover some additional hydrogen fluoride and to prevent air pollution.

Details of gas handling vary among U.S. manufacturers' plants. In one published process (37), the hydrogen fluoride gases are freed from solids and sulfuric acid mist by cyclone and countercurrent scrubbing in the lower section of a precondenser. Scrubbing fluid is recirculated after addition of some 20% oleum to combine with water. The hydrogen fluoride vapors, now low in water and sulfuric acid, are condensed as 99% hydrogen fluoride in an amount representing 98% of the production. This is redistilled to a purity above 99.9% hydrogen fluoride. The uncondensed gases are washed with fresh sulfuric acid to recover additional hydrogen fluoride. The gaseous effluent is now largely silicon tetrafluoride, which is absorbed in water and then recovered as 30–35% fluosilicic acid. This process is shown schematically in Figure 3.

Calcium sulfate residue from the kilns is commonly discarded, in view of availability of low-cost natural sources. Some, however, is neutralized with lime and sold for the manufacture of anhydrite cements.

Overall yield of hydrogen fluoride is typically 85–90%, based on calcium fluoride, and 75–85%, based on sulfuric acid.

Recovery from Phosphate Rock. Recognizing the enormous supply of fluorine values existing in phosphate rock reserves, and the large amount of fluorine values which are processed daily through fertilizer phosphate plants, many studies to produce hydrogen fluoride from this source have been made (38). Two economic hurdles exist: The fluorine values are released as silicon tetrafluoride, not conveniently convertible to hydrogen fluoride; and the collection of these fluorine values from many separated phosphate rock plants to provide feed for a hydrogen fluoride plant of economic capacity is expensive.

A proposed process (39) starts by reacting silicon tetrafluoride with recycled ammonium fluoride solution to form ammonium fluosilicate.

$$SiF_4 + 2\ NH_4F \rightarrow (NH_4)_2SiF_6$$

When this solution is neutralized with ammonia, silica precipitates and more ammonium fluoride is formed.

$$(NH_4)_2SiF_6 + 2\ H_2O + 4\ NH_3 \rightarrow SiO_2 + 6\ NH_4F$$

The ammonium fluoride solution (except that recycled) is evaporated to a salt concentration of 94–95%, when some conversion to ammonium bifluoride, NH_4HF_2, takes place by vaporization of ammonia. The evaporation continues until a salt concentration of 98% is reached, when the mixture solidifies at about 100°C. The solid mixture of ammonium fluoride and bifluoride, containing 60% of fluorine, is decomposed with 93–95% sulfuric acid at 180–190°C. Ammonium bisulfate is the principal component of the residue; this can be converted to ammonium sulfate by neutralizing with ammonia.

The economics of this process depend on a low-cost supply of silicon tetrafluoride, a premium market for precipitated silica (proposed, for example, as reinforcing pigment for rubber), and a local market for ammonium sulfate. The process is handicapped by a large filtration and evaporation load.

Materials of Construction. Generalizations regarding materials of construction where hydrogen fluoride and its aqueous solutions are to be handled have proved in numerous instances to be quite misleading, and laboratory corrosion tests must be looked upon only as the most general guides. In spite of these facts, readily available materials have been found to meet each specific problem encountered. The presence of impurities such as sulfur compounds and fluosilicic acid, and the degree of aeration, velocity, and temperature are important considerations. In the manufacture of hydrogen fluoride, steel generators have long been used satisfactorily, and lines and other equipment handling the gases from the generator may be of steel as long as acid condensing from these gases contains not less than 70% hydrogen fluoride. Weaker acids must be handled in nonferrous materials such as carbon, lead, bronze, or Monel. Lead is sensitive to the presence of fluosilicic acid and cannot be used when more than 2–3% of that acid is present. Monel is adversely affected by aeration and the presence of sulfur compounds. Natural rubber and neoprene are useful for strengths below 60% hydrofluoric acid, and particularly below 40%. Copper has been widely used for the distillation of hydrofluoric acid solutions to produce anhydrous hydrogen fluoride. Steel valves with Monel trim are generally satisfactory for anhydrous hydrogen fluoride, and bronze valves with Monel trim are suitable for aqueous hydrofluoric acid. A wide variety of materials have had limited use for gaskets, but polytetrafluoroethylene (PTFE) has proved to be most satisfactory, and pump and valve packings of PTFE have given excellent performance.

Handling and Precautions

Years of experience in the manufacture and use of hydrogen fluoride have shown that this material can be handled safely, provided that its special hazards are recognized and the necessary precautions are taken.

Anhydrous hydrogen fluoride has a sizable vapor pressure at room temperature and should be regarded as a liquefied gas under pressure. Anhydrous hydrogen fluoride, the higher concentrations of aqueous acid, and vaporized hydrogen fluoride are extremely corrosive to skin, eyes, mucous membrane, and lungs. In certain concentration ranges of hydrogen fluoride, burns of the skin may not be immediately evident, and may be manifested later by deep-seated ulceration.

First-aid treatments after contact of hydrogen fluoride with the skin start with immediate and thorough washing with water. The affected part should be immersed for at least one-half hour in cold 70% alcohol or cold saturated magnesium sulfate; or the cold solutions may be applied by saturated compresses changed at least every two minutes. If a physician is not immediately available, a paste of powdered magnesium oxide and glycerin, freshly prepared, may then be applied. Medical treatment may include infiltration of calcium gluconate solution beneath the skin (40). Following accidental inhalation of hydrogen fluoride vapors, the exposed person should be removed at once from the contaminated atmosphere, 100% oxygen should be administered, and the exposed person should avoid physical activity. After contact with eyes, first-aid treatment should be limited to thorough irrigation with clean water. In all cases of significant hydrogen fluoride exposure, a physician should be called (40).

In work with hydrogen fluoride, the proper use of protective clothing, goggles, face shields, and respiratory devices is important and a full knowledge of first-aid treatments is essential. Reference should be made to more detailed instructions, such as those published by the Manufacturing Chemists' Association (40).

Specifications, Packaging; Analysis

Bulk shipments of hydrogen fluoride are now limited largely to anhydrous acid and aqueous 70% solution. The lower concentration limit is set by compatibility with steel; concentrations below about 60% become corrosive to this material.

Aqueous 70% hydrogen fluoride has been supplied in 20-, 55-, and 100-gal steel drums. It now moves mostly in polyethylene-lined 30- and 55-gal steel drums; and in 6000-gal steel tank cars.

Anhydrous hydrogen fluoride is distributed in 100- and 200-lb steel cylinders, ICC type 4B-240; and in 6000- and 11,000-gal tank cars, types 105A300W and 105A500W. Freight classification is Hydrofluoric Acid, Anhydrous—White Label.

Laboratory packages of hydrogen fluoride are supplied at concentrations of 48, 60, and 70%, usually in polyethylene bottles or carboys. An especially pure electronic grade is supplied at 49%.

Anhydrous hydrogen fluoride is one of the purest chemicals in regular commercial distribution. A typical analysis (in %) is shown below.

HF	99.95
H_2SiF_6	0.015
SO_2	0.003
H_2SO_4	0.005
H_2O	0.02

The analysis of hydrogen fluoride and its aqueous solutions consists in the determination of hydrogen fluoride, water, and of the commonly associated impurities: silicon tetrafluoride or fluosilicic acid, sulfuric acid and fluorosulfuric acid, sulfur dioxide, and metals (chiefly iron). For manufacturing control, analyses are required of fluorspar for moisture, calcium carbonate, silica, and calcium fluoride, and of reactor residues for calcium fluoride, hydrogen fluoride, and sulfuric acid content.

Laboratory equipment for handling hydrogen fluoride during sampling and analysis is usually made of steel for high concentrations or of polyethylene for aqueous solutions. Samples of anhydrous hydrogen fluoride are most conveniently collected in small steel evacuated cylinders. It should be remembered that a cylinder should not be filled to more than about 85% of its water capacity.

The dilution of hydrogen fluoride for analysis requires care because of the heat evolved, the volatility of the hydrogen fluoride and hazards to the operator. A typical procedure involves the dilution of the sample with ice at the bottom of a cylindrical plastic pipe in the upper section of which, supported on a grid, is additional ice to absorb such vapors as are formed during dilution in the lower section.

Analyses frequently performed on hydrogen fluoride are as follows:

1. Total acidity—by titration of the diluted sample with standard alkali to a phenolphthalein end point.

2. Nonvolatile acidity (reported as H_2SO_4)—by evaporation of the diluted sample on a steam bath and titration of the residue with standard alkali to a phenolphthalein end point.

3. SO_2—by iodimetric titration of the diluted sample.

4. Iron—by evaporation of the diluted sample with excess sulfuric acid; fuming with sulfuric acid; reduction to ferrous iron; and colorimetric determination of iron with orthophenanthroline.

5. Silica (reported as H_2SiF_6)—by evaporation of the diluted sample on the steam bath in the presence of a small amount of NaCl; complexing fluoride with boric acid; formation of silicomolybdic acid; reduction to a blue heteropoly acid; and colorimetric estimation.

6. Water—by conductance measurement on the anhydrous acid.

Production and Price

Published production figures for hydrogen fluoride must be examined for the basis of presentation because of the large and changing proportion of captive use to merchant sales. A good index for hydrogen fluoride production is the consumption of acid-grade fluorspar, which is the source of nearly all hydrogen fluoride in the United States, and of which typically 98% is used for this purpose (41,42).

For a number of years in the 1950s, a large return flow of aqueous hydrogen fluoride into the merchant market was observed from the purchases of anhydrous hydrogen fluoride made by the U.S. Atomic Energy Commission. Typically, when 1 lb of anhydrous hydrogen fluoride entered the process for converting uranium oxide to uranium tetrafluoride, 0.5 lb of hydrogen fluoride passed through and was recovered as aqueous 70% solution. This was repurchased and sold as aqueous acid.

A conservative ratio of 2.2 lb of acid-grade fluorspar to 1 lb of hydrogen fluoride (stoichiometric for 100% calcium fluoride is a ratio of 1.99) gives the estimates of total U.S. production of hydrogen fluoride (100% basis) shown in Table 9, which is based on U.S. Bureau of Mines data for fluorspar consumed by hydrogen fluoride producers (41,42).

Table 9. Estimated U.S. Production of Hydrogen Fluoride,[a] averaged, short tons/yr

1927–1929	7,800	1952–1953	91,200
1930–1934	4,600	1954–1955	107,600
1935–1939	9,300	1956–1957	140,500
1940–1941	21,200	1958–1959	132,600
1942–1943	44,400	1960	169,400
1944–1945	54,300	1961	190,300
1946–1947	41,900	1962	166,500
1948–1949	44,600	1963	188,400
1950–1951	62,800	1964	219,600

[a] 100% HF content.

The list price for anhydrous hydrogen fluoride has varied from 16 to 18 ¢/lb in tank-car quantities. The price in April, 1965 was 18 ¢/lb for anhydrous hydrogen fluoride and 13.4 ¢/lb for the aqueous 70% acid (43).

Uses

The traditional use for hydrofluoric acid—the etching and polishing of glass—has not dwindled, but it has indeed been submerged by the requirements of other industries.

Again, because of the high proportion of hydrogen fluoride used captively, reliable use patterns are hard to fix precisely. The estimates in Table 10, however, give a reasonable perspective, and show trends.

Table 10. Estimated Utilization of Hydrogen Fluoride, %

	1957	1959	1961	1963
fluorinated organics	28	30	40	40
aluminum	40	39	33	35
atomic energy	12	13	12	10
petroleum	4	5	4	5
stainless steel	5	3	3	3
all other	11	10	8	7
Total	100	100	100	100

Since 1963 the demand for hydrogen fluoride in the manufacture of fluorinated organics for pressurizing gases (aerosol propellants), foaming agents, cleaning fluids, and plastics has continued to rise rapidly. The need for hydrogen fluoride in the manufacture of aluminum fluoride and synthetic cryolite rose sharply with the completion of new electrolytic pot lines for the manufacture of aluminum. Tapering-off of weapons stockpiling and the time lag in constructing forthcoming atomic power generating stations have resulted in a considerable drop in hydrogen fluoride needs for the manufacture of atomic energy feed materials. In the petroleum industry hydrogen fluoride has continued in use as an alkylation catalyst, to produce high-octane blending stock for automotive gasoline. Increased use of stainless steels has maintained requirements for hydrogen fluoride in pickling acids at a constant small proportion of the rising production of hydrogen fluoride. Other uses for hydrogen fluoride include sand removal from metal castings; preparation of fluorides and fluoborates; etching and polishing of glass; fluorosilicone products, manufacture of fluorine, and products derived therefrom; special dyes and pharmaceuticals; preparation of microelectronic circuits; laundry sours and stain removers; oil-well acidizing; and mineral analysis.

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