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HYDROGEN

As the starting point for most fluorine products and in volume of production, hydrogen fluoride [*7664-39-3*] is the most important manufactured compound of fluorine. Both anhydrous hydrogen fluoride and its aqueous solutions are sold for use directly and as intermediates in making other fluorine-containing materials. The aqueous solution is usually called hydrofluoric acid; the anhydrous compound is preferably called hydrogen fluoride.

Anhydrous hydrogen fluoride is a colorless liquid or gas (bp 19.54°C), completely 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. The compound can cause human injury in any form of contact, and informed control of hazards in handling and use must be observed.

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

The earlier quite limited uses for hydrofluoric acid, such as glass etching and polishing, foundry scale removal, and minor production of metal fluorides, predominated until the 1930s. In the period 1935 to 1940, the large increase in aluminum production brought an equivalent requirement for hydrogen fluoride, employed captively for aluminum refining. Anhydrous hydrogen fluoride was first made by Frémy in 1856 (2), but there was no significant commercial manufacture until 1931 when the first bulk shipment was made by Sterling Products Company for use in making chlorofluorohydrocarbons as refrigerating fluids. 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); manufacture of chlorofluorohydrocarbons for use in pressurized packaging (USDA, 1942); and the manufacture of uranium fluorides (Manhattan District Engineers, 1942). The growth of all of these industries, and of stainless steel pickling and of fluorine-containing plastics brought the volume of hydrogen fluoride production to the current high levels.

Physical Properties

The properties of anhydrous hydrogen fluoride are summarized in Tables 1–2. Additional data are available in the references cited. Enthalpy–temperature and entropy–temperature diagrams are shown in refs. 9 and 19; spectrographic data in ref.

Table 1. Properties of Anhydrous Hydrogen Fluoride

Property	Value	Reference
formula weight	20.006	
composition, wt %		
H	5.038	
F	94.96	
molecular weight		
saturated vapor at boiling point	78.24	3
saturated vapor at 100°C	49.08	3
boiling point at 101.3 kPa (1 atm), °C	19.54	4
melting point, °C	−83.55	5
cryoscopic constant K_f, mol/kg solvent, °C	1.52	5
ebullioscopic constant K_b, mol/kg solvent, °C	1.9	6
density		
liquid at 0°C, g/cm^3	1.002	
liquid at 25°C, g/cm^3	0.9576	7
saturated vapor at 25°C, mg/cm^3	3.553	3
saturated vapor at 34°C, mg/cm^3	3.979	3
vapor pressure at 25°C, MPa[b]	122.9	3
heat of vaporization at boiling point, 101.3 kPa (1 atm), J/mol[c]	7493	4
heat of fusion at melting point, J/mol[c]	3931	8
heat capacity, constant pressure		
liquid at 16°C, J/(mol·°C)[a,c]	50.6	8
vapor at 22°C, 101.3 kPa (1 atm), J/(mol·°C)[a,c]	456	4
heat of formation		
ideal gas at 25°C, kJ/mol[c]	−272.5	9–10
free energy of formation		
ideal gas at 25°C, kJ/mol	−274.6	9–10
entropy		
ideal gas at 25°C, J/(mol·°C)[a,c]	173.7	9–10
critical temperature, °C	188	11
critical pressure, MPa[b]	6.480	11
critical density, g/cm^3	0.29	11
viscosity, mPa·s (= cP) at 0°C	0.256	12
surface tension, mN/m (= dyn/cm) × 10^{-4} at 0°C	10.1	
refractive index,		
liq, 58930 nm, 25°C	1.1574	13
molar refractivity, cm^3	2.13	13
dielectric constant, at 0°C	83.6	14
dipole moment, HF molecule, C·m[d]	6.10×10^{-30}	15
bond length, H–F, nm	9.2	6
ionic character, %	43	16
electric conductivity, $(\mu\Omega\text{·cm})^{-1}$ at 0°C		6

[a] mol = 20.01 g.
[b] To convert MPa to atm, divide by 0.101.
[c] To convert J to cal, divide by 4.184.
[d] To convert C·m to debye, divide by 3.336×10^{-30}.

Table 2. Temperature Variation of Physical Properties of Anhydrous Hydrogen Fluoride

Temperature, °C	Vapor pressure, kPa[a,b]	Density, g/cm³ Saturated vapor[c]	Density, g/cm³ Liquid[d]	Heat of vaporization, J/mol[e,f,g]	Heat capacity J/(mol·°C)[f] Liquid C_p[g]	Heat capacity J/(mol·°C)[f] Vapor C_v[h]	Heat capacity J/(mol·°C)[f] Vapor C_p[i]
−70	1.39		1.176		43.26		
−60	2.52		1.149		43.59		
−50	4.62		1.123		44.10		
−40	7.86		1.098		44.77		
−30	12.96		1.073		45.48		
−20	20.68		1.048		46.44		
−10	32.06		1.025		47.49		
0	48.26	0.00215	1.003	7042	48.61		
10	71.01	0.00252	0.98		49.96		
20	103.42	0.00317	0.968	7473	51.21	46.27	250
30	146.17	0.00398	0.945			47.69	805
40	203.40	0.00498	0.928			49.12	824
50	274.42	0.00619	0.908			50.54	350
60	370.95	0.00765	0.888			51.96	120
70	489.54	0.00939	0.867			53.38	50
80	641.23	0.01144	0.844			54.81	40
90	820.50	0.01385	0.820			56.23	30
100	1054.93		0.796			57.57	30

[a] To convert kPa to psi, multiply by 0.145.
[b] Refs. 3, 7, and 17.
[c] Ref. 3.
[d] Ref. 7.
[e] Calorimetric.
[f] To convert J to cal, divide by 4.184.
[g] Ref. 8.
[h] Ref. 7.
[i] Ref. 18.

9; and a critical review of thermodynamic properties of gaseous HF is given in ref. 4.

The properties of aqueous solutions of hydrogen fluoride are given in Tables 3–9, and Figures 1–2. An entropy-concentration diagram and adiabatic HF absorption diagrams are provided in refs. 29–30.

Table 3. Physical Properties of Aqueous 70% Hydrogen Fluoride

Property	Value	Reference
boiling point at 101.3 kPa (1 atm), °C	66.4	17
freezing point (solid phase is $HF.H_2O$), °C	−69	18
vapor pressure at 25°C	20 kPa (2.9 psia)	20
density at 25°C, g/cm³	1.22	

Table 4. Density of Aqueous Hydrogen Fluoride, g/cm³ [a]

Hydrogen fluoride, wt %	Temperature, °C			
	0	20	40	60
0	1.000	0.998	0.992	0.983
20	1.080	1.070	1.055	1.035
40	1.159	1.135	1.12	1.10
60	1.235	1.21	1.18	1.15
65	1.248	1.225	1.19	1.16
70	1.258	1.23	1.195	1.16
75	1.262	1.23	1.195	1.155
80	1.259	1.22	1.18	1.135
85	1.240	1.18	1.135	1.11
90	1.178	1.105	1.06	1.04
100	1.003	0.968	0.928	0.888

[a] Refs. 7, 21–22.

Table 5. Partial Pressure of Hydrogen Fluoride over HF-H_2O Solutions, Pa [a,b]

Hydrogen fluoride, wt %	Temperature, °C					
	0	20	40	60	80	100
0	0	0	0	0	0	0
10	4.0	18	68	216	500	1,490
20	12	55	201	633	1,760	4,360
30	40	169	595	1,790	4,760	11,400
50	488	1,653	4,770	12,200	27,900	58,700
70	5,490	15,370	39,300	88,200	108,600	343,000
100	48,500	103,041	202,000	370,300	640,010	1,050,000

[a] Ref. 20.

[b] To convert Pa to mm Hg, multiply by 7.5×10^{-3}.

Chemical Properties

The chemistry of hydrogen fluoride is dominated by five features: the great strength of the hydrogen–fluorine bond; the significant strength of secondary hydrogen bonds to fluorine; the absence of oxidation states of fluorine other than −1; strong polymeric association in the solid, liquid, and gas states; and a strong acid character in apparent contradiction with a low ionic dissociation in water solution.

The hydrogen fluoride molecule remains intact up to remarkably high temperatures. From the free energy of formation of hydrogen fluoride molecule and the heat capacities of hydrogen fluoride and its elements, it is calculated that only 40% is dissociated into hydrogen atoms and fluorine atoms at 4000°C. Next to N_2 and CO, HF is the most stable diatomic molecule. This fact, plus its high heat of formation, gives the combination of hydrogen and fluorine the highest specific impulse available to rocketry when stable chemical species are used (31) (see Explosives and propellants).

Above 200°C, the vapor of hydrogen fluoride is approximately monomolecular, but as the temperature is lowered, hydrogen bonding leads to chains of increasing

Table 6. Partial Pressure of Water over HF-H_2O Solutions, Pa[a, b]

Hydrogen fluoride, wt %	Temperature, °C					
	0	20	40	60	80	100
0	610	2,340	7,378	19,912	47,330	101,300
10	594	2,130	6,520	17,500	41,600	90,500
20	484	1,750	5,370	14,400	34,500	75,400
30	363	1,230	4,080	11,000	26,500	58,100
50	101	397	1,310	3,760	9,580	21,990
70	nil	13				0
100	0	0	0	0	0	0

[a] Ref. 20.

[b] To convert Pa to mm Hg, multiply by 7.5×10^{-3}.

Table 7. Heat of Dilution of Aqueous Hydrogen Fluoride Solution[a]

Hydrogen fluoride, wt %	Heat of dilution[b], J
0	970
10	937
20	912
30	874
40	820
50	736
60	623
70	502
80	380
90	217
100	0

[a] Ref. 23.

[b] Heat evolved when one gram of anhydrous HF is diluted with water to the concentration shown. To convert J to cal, divide by 4.184.

length, thus: —F—H—F—H—F—H—. Although these secondary hydrogen bonds are relatively weak (about 25 kJ/mol (6 kcal/mol) of H—F (32)), they have a marked effect on the properties of hydrogen fluoride. Thus the boiling point of hydrogen fluoride is much higher then those of the other hydrogen halides (HF, 19.5°C; HCl, −84°C; HBr, −67°C; HI, −35°C). The effects of hydrogen bonding persist into the vapor and cause large deviations from ideal gas behavior. Near its boiling point, hydrogen fluoride is one of the most imperfect gases known. In the solid state, hydrogen fluoride exists as zig-zag chains of molecules with spacing and angles as shown in Figure 3. In the liquid and gas states, rotation about bonds removes the conformation regularity. At the same time, the length of the hydrogen-bonded polymers decreases, and near the boiling point the number of units in the liquid and gas phases reaches an average of about 3.5 (12). The angle H—F—H, ca 120°, is close to the internal angle of a hexagon, and probably many of the molecular aggregates have the ring structure H_6F_6. Since fragments of different lengths are present, it is not meaningful to designate the formula as H_6F_6 or as H_2F_2, as is sometimes done. Because the mobile equilibria between the hydrogen fluoride polymers may have a significant time constant, measurements by dynamic and static methods may give different results.

Table 8. Specific Conductivity of Aqueous Hydrogen Fluoride Solutions, at 0°C, 1/(Ω-cm)

Hydrogen fluoride, wt %	Conductivity
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	$<1.6 \times 10^{-6}$

[a] Refs. 24–25.

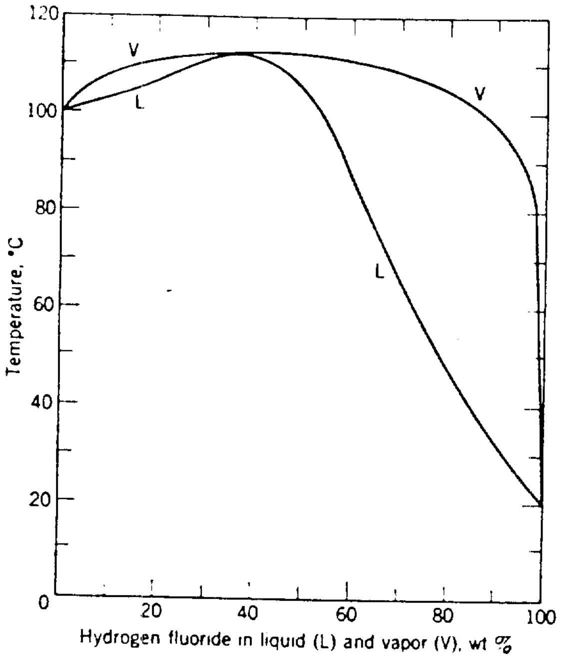

Figure 1. The boiling and liquid–vapor compositions of the system HF.H_2O (26–27).

Although hydrogen fluoride in water solution is weakly dissociated (into H^+ and $(HF)_{x-1}F^-$), anhydrous hydrogen fluoride and high aqueous concentrations of HF are very strong acids in the proton donor sense (Brønsted-Lowry concept (33)). Thus the Hammett acidity function H_0 approaches −11. Since the Hammett scale is related to pH and is in a sense an extension of the pH scale, the high negative value of H_0 shows anhydrous hydrogen fluoride to be in the class of superacids. Addition of antimony

Table 9. Liquid and Vapor Compositions of Aqueous Solutions of Hydrogen Fluoride at the Boiling Points, 101.3 kPa (1 atm)[a] [b]

wt % HF in liquid	0.0	10.0	20.0	30.0	40.0	50.0	60.0	70.0	80.0	90.0	100.0
wt % HF in vapor	0.0	2.0	6.77	19.3	43.5	74.3	95.5	98.8	99.2	99.5	100.0
boiling point, °C	100.0	102.8	106.8	110.3	112.1	105.1	88.0	66.1	47.6	32.0	19.54

[a] Ref. 26.

[b] There is a constant-boiling composition at 38.26% HF; boiling point 112°C at 98.6 kPa (740 mm Hg).

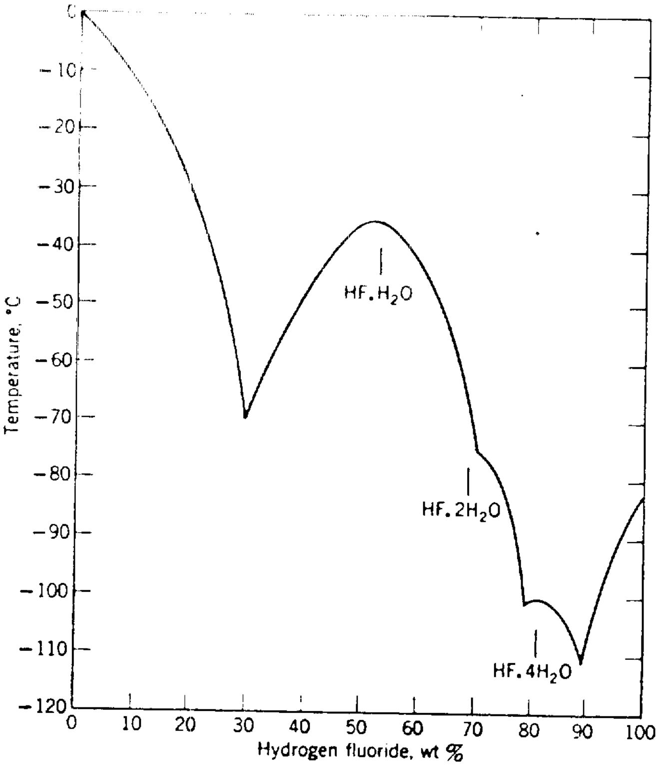

Figure 2. Freezing points of aqueous hydrogen fluoride solutions (28).

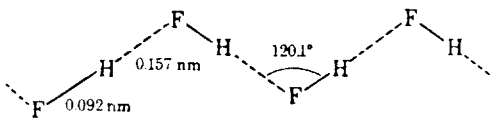

Figure 3. Conformation of hydrogen fluoride in the solid state (6).

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).

The strong catalytic activity of anhydrous hydrogen fluoride is attributed to its ability to donate a proton, as in the dimerization of isobutylene:

$$CH_2{=}C(CH_3)_2 + HF \rightarrow (CH_3)_3C^+ + F^-$$

$$(CH_3)_3C^+ + CH_2{=}C(CH_3)_2 \rightarrow (CH_3)_3C{-}CH_2C^+(CH_3)_2$$

$$\rightarrow (CH_3)_3\,CCH{=}C(CH_3)_2 + H^+$$

Because of its very high dielectric constant, its relatively high boiling point, long liquid range, and low viscosity, anhydrous hydrogen fluoride is an excellent solvent for ionic fluorides (Table 10). Generally, the soluble fluorides act as simple bases, fully ionized and increasing the concentration of HF_2^-:

$$HF + KF \rightarrow K^+ + HF_2^-$$

Table 10. 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	5.60
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. 12.

Many metal fluorides can then be isolated from hydrogen fluoride solution as salts of the HF_2^- anion.

The solubility of organic compounds in anhydrous hydrogen fluoride is often related to their proton-accepting capability. Most substances containing oxygen, nitrogen, or sulfur atoms that are not coordinatively saturated offer a lone electron pair capable of binding protons and are usually very soluble (6,35). Addition of a proton from the hydrogen fluoride may cause subsequent reactions including polymerization. On the other hand, the organic material can often be recovered unchanged from the hydrogen fluoride. In the simpler cases, ionic species are present and the solutions are electrically conducting:

$$C_2H_5OH + HF \rightarrow C_2H_5OH_2^+ + F^-$$

This behavior is the basis of electrochemical fluorination to produce a wide range of highly fluorinated products (36).

Anhydrous hydrogen fluoride is an active dehydrating agent. Wood and paper are charred on contact, and aldehydes undergo condensation by elimination of water. Anhydrous hydrogen fluoride is less powerful than sulfuric acid in this respect. For example, hydrogen fluoride does not rapidly dehydrate primary alcohols.

The small size of the fluoride ion permits it to participate in coordination structures of high rank. For example, tantalum and niobium form stable hexafluorotantalate and hexafluoroniobate ions and hydrogen fluoride will attack these usually acid-resistant metals. The attack of hydrofluoric acid on silicates is a special case. Ready formation of hexafluorosilicate ion is further promoted by decomposition to volatile silicon tetrafluoride.

As noted above, hydrogen fluoride in water solution is a weak acid. Two dissociation constants need to be considered:

$$K_1 = \frac{[H^+][F^-]}{[HF]} = 6.46 \times 10^{-4}\,M$$

$$K_2 = \frac{[HF_2^-]}{[HF][F^-]} = 5 \text{ to } 25\,M$$

The primary acid dissociation constant, K_1, shows hydrofluoric acid to be only about as strong as formic acid, whereas the other hydrohalic acids are almost completely dissociated. The apparent contradiction with hydrogen fluoride as a powerful proton donor has been discussed in a number of ways. The reduction in availability of protons from the hydrogen-bonded polymer should not be significant for the degree of polymerization that is likely, since the dissociation constants indicate that the hydrogen ion concentration in aqueous hydrofluoric acid is about 1/200th that in hydrochloric acid. A detailed thermodynamic comparison of the hydrohalic acids shows that the enthalpy changes for dissociation of the acids in water solution are not very different. However, there is a large negative entropy of hydration of fluoride ion in the case of hydrofluoric acid. This makes the Gibbs free energy change for the overall dissociation process actually positive, and the degree of dissociation in water solution is therefore small (37).

Manufacture

The preferred raw materials for the manufacture of hydrogen fluoride are acid-grade fluorspar and sulfuric acid:

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

The rate and yield in commercial apparatus is influenced by the purity and fineness of the fluorspar, the concentration of the sulfuric acid, the ratio of sulfuric acid to fluorspar, the temperature of the reaction mixture, and the intimacy of mixing of the acid and spar. Since fluorine values dominate the raw material costs, the operating factors are optimized to give maximum yield of hydrogen fluoride based on fluorspar.

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

Screen analysis: 2% on 149 μm (110 mesh), 13% on 74 μm (200 mesh), 55% through 44 μm (325 mesh) (38).

Chemical analysis:

CaF_2	minimum 96.5 to 98%
SiO_2	maximum 1.0%
S	maximum 0.05%
H_2O	maximum 0.05%
$CaCO_3$	principal remainder

Silica is a highly objectionable contaminant, since each 0.45 kg of silica consumes 1.18 kg fluorspar and 1.50 kg 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 troublesome in consuming sulfuric acid, in causing foaming in the generator, and in contributing carbon dioxide to the gas stream where it is a noncondensable diluent of the hydrogen fluoride. Sulfur-bearing contaminants of fluorspar, such as galena or pyrites, may generate hydrogen sulfide or sulfur dioxide, contaminating the hydrogen fluoride, and sometimes causing sulfur deposits in the gas handling equipment.

Other conditions being constant, the finer the fluorspar, the readier is the liberation of hydrogen fluoride from the spar and the better the yield. Fluorspar of the screen analysis given above has been used directly in the hydrogen fluoride kilns with good yields. Some manufacturers grind this material further. Such additional grinding is an expensive operation involving some handling loss of fluorspar, and the effect of this step must be analyzed on the basis of the improvement in yield it produces compared with other means of obtaining the same improvement.

Sulfuric acid of a concentration as low as 93% or as high as 99% has been used in hydrogen fluoride manufacture. The more dilute acid gives a more fluid reacting mass during initial mixing and a smoother liberation of hydrogen fluoride. Two factors offset this benefit: (*1*) the more dilute sulfuric acid is much more corrosive to the generator, and (*2*) the greater amount of water will leave with the hydrogen fluoride and increase problems in condensation.

The ratio of sulfuric acid to fluorspar charged to the generator is seldom the stoichiometric ratio. Depending on the relative cost of the two ingredients, one or the other is used in slight excess. In U.S. practice, economic operation demands the maximum release of hydrogen fluoride from the fluorspar and justifies the use of a 5–10% excess of sulfuric acid. A greater excess of sulfuric acid will result in a "wet" calcium sulfate residue, which may be strongly fuming unless the sulfuric acid is driven out of the generator with the hydrogen fluoride by high operating temperatures.

Because the reaction of calcium fluoride and sulfuric acid is endothermic, heat must be supplied. The theoretical heat absorbed is 1400 kJ/kg (603 Btu/lb). To effect a release of over 98% of the fluorine in the fluorspar, the reaction time is normally 30–60 minutes at 200–250°C, with the hydrogen fluoride leaving the generator at 100–150°C. The lowest operating temperatures at which good yields are obtained are desirable to reduce the energy requirement and to minimize corrosion of the generator.

The diffusion of sulfuric acid through the product layer of calcium sulfate to the unreacted core seems to be a significant barrier to the progress of the reaction (39). Therefore, constant and effective mixing is important. In present practice, hydrogen fluoride generators may be rotary kilns, horizontal and externally fired, with spar fed continuously at the forward end by a screw conveyor. Acid is also introduced 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. These consist of a long horizontal vessel of U-shaped cross section carrying a central shaft extending the full length and equipped with mixing and conveying paddles. As in the rotary kiln, spar and acid move concurrently down the length of the reactor. In recent constructions, a combination of the two types of reactors is used. A stationary prereactor receives spar and heated sulfuric acid and feeds the well-mixed but incompletely reacted components into a heated rotary kiln. This enables the kiln to be made of lower cost steel and is said to give improved yields (40).

Since hydrogen fluoride is readily absorbed by water, early manufacturers made an aqueous solution of the gases from the generator and prepared strong acid by fractionation, or when strengths above the atmospheric azeotrope (38%) were needed, by distillation with sulfuric acid. Current requirements are mainly for the anhydrous compound, and manufacturers have succeeded in controlling conditions in the generator to supply effluent gas low enough in water and noncondensables to permit direct condensation, with reboiling to give anhydrous hydrogen fluoride. Vent gases must still be scrubbed with water to recover additional hydrogen fluoride and to prevent air pollution.

Details of gas handling vary among manufacturers. In one published process (41), the hydrogen fluoride gases are freed from solids and sulfuric acid mist by cyclone separation and countercurrent scrubbing in the lower section of a precondenser. Scrubbing fluid is recirculated through the kiln after addition of 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 from the kiln. 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 final gaseous effluent is largely silicon tetrafluoride, which is absorbed in water and recovered as 30–35% fluorosilicic acid. The overall process is shown schematically in Figure 4.

Calcium sulfate from the kilns is commonly discarded, in view of the general availability of natural gypsum. Some, however, is neutralized with lime and sold for the manufacture of anhydrite cements.

The overall yield of hydrogen fluoride is 85–95% based on calcium fluoride; and 75–85% based on sulfuric acid. Production of one metric ton of hydrogen fluoride typically requires 1750 kg of steam at 1.03 MPa (150 psi) pressure, 220 kW·h of electricity, 1.5 GJ (3.6×10^5 kcal) of refrigeration at −10°C, 9.6 GJ (2.3×10^6 kcal) fuel, over 12 m^3 (ca 3000 gal) of process water, and 116 m^3 (ca 30,000 gal) of cooling water (42).

Recovery from Phosphate Rock. Recognizing the enormous supply of fluorine values existing in phosphate rock reserves, and the large amount of fluorine values that are processed daily through phosphate fertilizer plants, many studies have evaluated the feasibility of obtaining hydrogen fluoride from this source. Two economic obstacles exist: the fluorine values are released as silicon tetrafluoride, not easily convertible to hydrogen fluoride; and the collection of these fluorine values from many scattered fertilizer plants to provide feed for a hydrogen fluoride plant of economic capacity is expensive. Thus a hydrogen fluoride plant typically needs to produce at least 22,700 metric tons per year to be economically useful, but most fertilizer plants can supply no more than 9000 t of hydrogen fluoride equivalent annually.

A proposed process starts by the reaction of silicon tetrafluoride with recycled ammonium fluoride solution to form ammonium fluorosilicate:

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

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 which is recycled, is evaporated to a salt concentration of 94–95%. At this concentration, some conversion to ammonium bifluoride, NH_4HF_2, takes place by evaporation of ammonia. The evaporation is continued until a salt concentration of 98% is reached; the mixture solidifies at about 100°C. The solid mixture of ammonium fluoride and ammonium bifluoride, containing 60% fluorine is decomposed with 93–95% sulfuric acid at 180–190°C. The residue is mainly ammonium bisulfate, which 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, and a local market for ammonium sulfate. The process is handicapped by a large filtration and evaporation load.

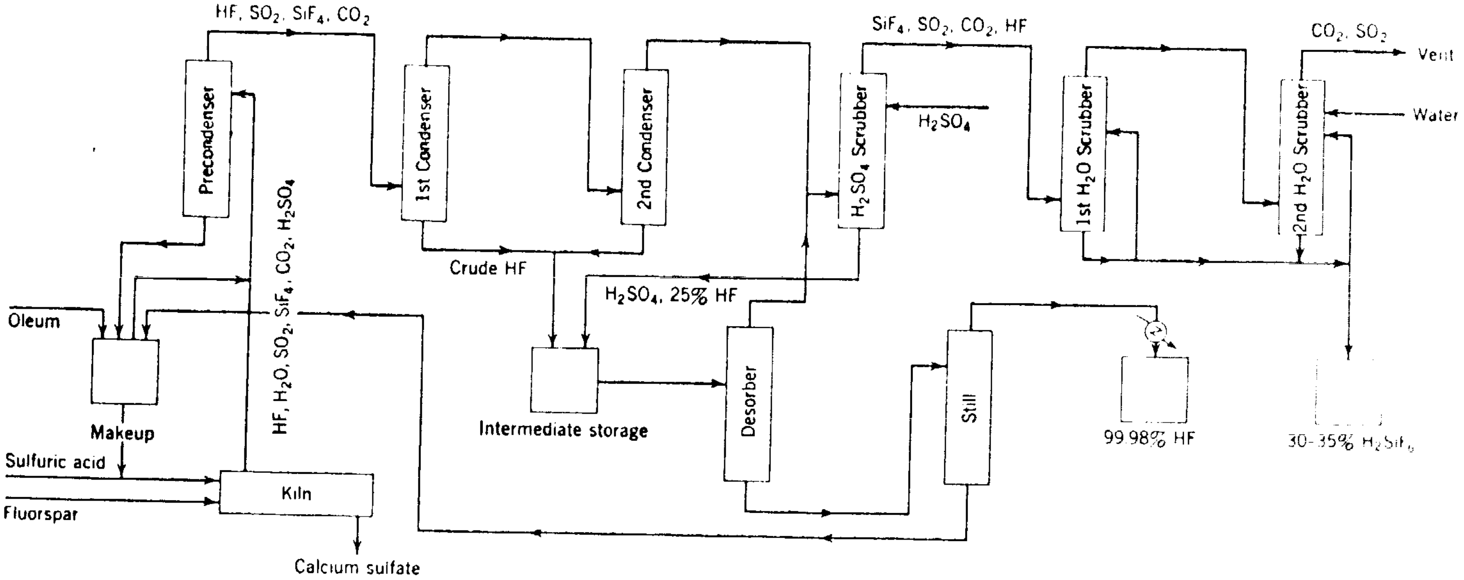

Figure 4. Schematic flow diagram for the manufacture of hydrogen fluoride.

A process developed by the U.S. Bureau of Mines starts from fluorosilicic acid:

$$3\ SiF_4 + 2\ H_2O \rightarrow 2\ H_2SiF_6 + SiO_2$$

Lime and silica are added:

$$3\ Ca(OH)_2 + H_2SiF_6 \rightarrow 3\ CaF_2 + SiO_2 + 4\ H_2O$$

The calcium fluoride and silica precipitate is filtered and pelletized. The pellets are fed to a 1050°C rotary kiln with steam. The reaction produces a gas stream of hydrogen fluoride, water vapor and a residue of calcium silicate:

$$CaF_2 + H_2O + SiO_2 \rightarrow CaSiO_3 + 2\ HF$$

Recovery of 80% of the fluorine in the fluorosilicic acid as hydrogen fluoride is claimed.

Buss, Ltd. has piloted a process in which fluorosilicic acid from the scrubber towers of fertilizer manufacture is concentrated, then vaporized as an $HF–SiF_4–H_2O$ mixture. The gases enter the middle of an absorption column. In the upper half, an organic solvent selectively absorbs hydrogen fluoride. Pure hydrogen fluoride vapors entering the bottom of the column strip small amounts of water and silicon tetrafluoride from the solvent. The hydrogen fluoride is desorbed from the solvent in a vacuum evaporator, liquefied, and purified by two-stage rectification. Silicon tetrafluoride in the overhead gas from the absorber is hydrolyzed to silica and fluorosilicic acid. The latter is recycled, and the silica can be sold for a credit to the processing costs.

Materials of Construction. Generalizations regarding materials of construction where hydrogen fluoride and its aqueous solutions are to be handled have sometimes proved misleading, and laboratory tests give at best only general guidance. Nevertheless, readily available materials have been found to meet each problem encountered. The presence of impurities such as sulfur compounds and fluorosilicic acid, and the aeration, velocity, and temperature of the hydrogen fluoride are important considerations in determining the appropriate material. In the manufacture of hydrogen fluoride, steel generators are successfully used. Pipes and other equipment handling the gases from the generator may be of steel as long as acid condensation from these gases is 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 fluorosilicic 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%, and particularly below 40%. Copper has been used for distillation of aqueous hydrogen fluoride solutions. For exacting laboratory work with aqueous solutions containing fluorosilicic acid, silver apparatus is excellent (26). Steel valves with Monel stems are generally satisfactory for anhydrous hydrogen fluoride, and bronze valves with Monel stems are suitable for aqueous hydrofluoric acid. A wide variety of materials have had limited use for gaskets, but polytetrafluoroethylene (PTFE) has proved to be the most satisfactory. Pump and valve packings of PTFE have given excellent performance. Lower strengths of aqueous hydrofluoric acid can be shipped and stored in polyethylene jugs or in polyethylene drums and steel overpacks (43). Glass and silicate ceramics are, of course, never acceptable.

Economic Aspects

In 1979, hydrogen fluoride was being manufactured in the United States by five companies in nine plants. Capacities of North American producers are shown in Table 11 (44). Plant capacity ranged from 5400–68,000 metric tons per year, with an average of 27,000 t/yr. One U.S. company operated a 68,000 t/yr hydrogen fluoride plant at Matamoros, Mexico; and another U.S. company has merchant capacity for 45,000 t in Canada (45).

Published production figures for hydrogen fluoride must be examined for the basis of presentation because of the large and changing proportion of captive uses to merchant production. 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 about 98% is used for this purpose (46). A conservative ratio of kg acid-grade fluorspar to 0.45 kg hydrogen fluoride (stoichiometric ratio for 100% CaF_2 is 1.95) gives the estimates of total U.S. production of hydrogen fluoride (100% basis) shown in Table 12 (45–46). Worldwide production is estimated in Table 13.

The growth rate of hydrogen fluoride production in the United States has dropped from about 10% annually in the 1940s and 1950s to 5% in the 1960s, to 3% in the early 1970s, and to the low current rate of about 0.5%. A sharp decrease in demand for hydrogen fluoride occurred in 1978 when the United States prohibited the use of chlorofluorocarbon gases in pressure packaging because of their supposed adverse effect on the concentration of ozone in the high altitude atmosphere (48–49) (see Air pollution; Ozone). This environmental question remains controversial. In the future the ban may be lifted, or it may be extended to prohibit the use of chlorofluorocarbons as refrigerants. Greater efficiency in the use of hydrogen fluoride in the aluminum industry, as described below, and production of aluminum fluoride and cryolite directly from fluorosilicic acid has further slowed the increase in demand for hydrogen fluoride. Other demands for hydrogen fluoride are about one-fourth of total use, and are likely to rise about in proportion to economic activity. Estimates of future growth in hydrogen

Table 11. North American Producers and Capacities of Hydrogen Fluoride, 1000 Metric Tons[a]

Producer	1979 capacity, 10^3 t
Allied	132
DuPont	68
Alcoa	50
Pennwalt	23
Harshaw	16
Essex	10
Alcan	45
Química Fluor	68
Industria Química de México	14
Quimobásicos	3
Total	*429*
Number of producers	*10*

[a] Ref. 44.

Table 12. U.S. Consumption of Hydrogen Fluoride Averaged, 1000 Metric Tons

1930–1939	6.3
1940–1949	37
1950–1959	97
1960–1964	165
1965–1969	253
1970	295
1971	303
1972	319
1973	332
1974	340
1975	386
1976	349
1977	293
1978	324

Table 13. World Production of Hydrogen Fluoride[a] 1973, 1000 Metric Tons × 10^3

United States[b]	240
Soviet Bloc	100
France	73
Canada	72
FRG	81
Japan	65
Italy	59
United Kingdom	34
Mexico	54
Norway	18
Spain	15
People's Republic of China	7
India	5
Netherlands	6
Australia	5
Republic of South Africa	0.9
Total	838

[a] Ref. 47.

[b] U.S. figure differs from Table 10 mainly in the omission of imports.

fluoride consumption range from 1–4% annually. The lower rate is more probable, unless a major new use for fluorine chemicals arises. No such new use is now in sight.

Hydrogen fluoride prices have risen with general inflation (Table 14). Since no

Table 14. Price of Hydrogen Fluoride and Hydrofluoric Acid; Tank Cars, ¢/kg

	1950	1960	1970	1974	1975	1976	1977	1978	1979
anhydrous HF	36.4	39.7	54	81.6	90.4	93.7	98.1	98.1	98.1
hydrofluoric acid 70%	31.5	29.5	39.7	75.2	65.7	69.4	74.5	74.5	77.2

shortage of raw material is evident, and since manufacturing capacity is adequate, no extra-inflationary price increases are expected.

Health and Safety Factors

Hydrogen fluoride, anhydrous or aqueous, is a dangerous substance. However, years of experience in its manufacture and use have shown that it can be handled safely, provided the special hazards are recognized and the necessary precautions are taken. Excellent manuals describing equipment and procedures for the safe handling of hydrogen fluoride are available from the major manufacturers and from the Chemical Manufacturers' Association (9,43,50–53).

Anhydrous hydrogen fluoride, vaporized hydrogen fluoride, and even rather dilute solutions of the aqueous acid can be extremely damaging to skin, eyes, mucous membrane, and lungs. In certain concentration ranges of hydrogen fluoride, burns of the skin that are not immediately evident may be manifested later by deep-seated ulceration.

First-aid treatment after contact of hydrogen fluoride with the skin starts with immediate and thorough washing with water. To slow penetration of fluoride ion through the skin, the affected part should be immersed for at least one-half hour in ice-cold 7% alcohol, or in ice-cold saturated magnesium sulfate solution, or in ice-cold 0.13% benzalkonium chloride. Alternatively, 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 glycerol, freshly prepared, may then be applied. Medical treatment may include infiltration of calcium gluconate solution beneath the skin (53). Accidental inhalation of hydrogen fluoride vapors should be treated by immediately removing the exposed person from the contaminated atmosphere, and by administering 100% oxygen. The exposed person should avoid physical activity. After contact with eyes, first-aid treatment should be limited to thorough irrigation with clean water. Any significant hydrogen fluoride exposure is a medical emergency, and a physician should be called.

In work with hydrogen fluoride, the proper use of protective clothing, gloves, goggles, face shields, and respiratory devices is important, and a full knowledge of first-aid procedures is essential. Reference should be made to detailed instructions, such as those published by the Chemical Manufacturers' Association (53).

A danger not always recognized in working with hydrogen fluoride in the presence of metals is the chance of generating hydrogen, and the possibility of explosion, if the concentration of hydrogen fluoride drops below 60–65% through accidental or improper addition of water. Systems for dilution of hydrogen fluoride must be protected against return flow of diluted acid.

The recommended limit for occupational exposure to hydrogen fluoride in air is a time-weighted average of 1.5 mg HF/m^3 air for up to a 10-h workday, 40-h work-week; with a ceiling of 60 mg/m^3 averaged over 5 min (54).

Specifications, Packaging, and Analysis

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

The primary suppliers of anhydrous fluoride ship in tank cars of 20–91 t capacity, specification 105A300 or 114A40; in tank trucks holding 20 t, specification MC311 or MC312. The product may be repackaged into steel cylinders holding 8–907 kg. The aqueous 70% solution is shipped in tank cars of 32–80 t capacity, in tank trucks of 20 t capacity, and in polyethylene-lined drums holding 114 or 208 L (30 or 55 gal). Both the anhydrous and aqueous acid must be labeled: Corrosive Liquid—White Label (43,50–52). Reagent grade hydrofluoric acid is supplied in polyethylene bottles or carboys at 48%, and an especially pure electronic grade is made to 49%.

Anhydrous hydrogen fluoride is one of the purest chemicals in regular commercial distribution. A typical analysis is (55):

HF	99.99%
H_2SiF_6	0.001
SO_2	0.003
H_2SO_4	0.005
H_2O	0.0004

The analysis of hydrogen fluoride and its aqueous solutions includes the determination of hydrogen fluoride and water and of the commonly associated impurities: fluorosilicic acid, sulfuric and fluorosulfonic acids, sulfur dioxide, and metals (chiefly iron). For manufacturing control, fluorspar must be analyzed for moisture, calcium carbonate, silica, and calcium fluoride; and reactor residues, for calcium fluoride, hydrogen fluoride, and sulfuric acid.

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 can be collected in evacuated steel cylinders. A cylinder should not be filled beyond 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 the hazards to the analyst. A typical procedure involves dilution with ice at the bottom of a cylindrical pipe in the upper section of which, supported on a grid, is additional ice to absorb any vapors. Frequently performed analyses include the following:

(*1*) Total acidity: by titration of the diluted sample with standard alkali to the phenolphthalein end point.

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

(*3*) Sulfur dioxide: 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 with *o*-phenanthroline.

(*5*) Silica (reported as H_2SiF_6): by evaporating the diluted sample in the presence of a small amount of sodium chloride; complexing fluoride with boric acid; formation of silicomolybdic acid; reduction to a blue heteropoly acid; and colorimetric estimation. An alternative procedure involves redissolving the residue, adding potassium chloride, and exact neutralization at 10°C, followed by titration with standard alkali at 60°C.

(*6*) Water: by conductance measurement on the anhydrous acid; or by Karl Fischer procedure.

(7) Total fluoride: by difference from the above measurements, or by the use of a fluoride electrode (56).

Details of some of these methods and of sampling procedures are given in ref. 52.

Uses

The traditional use for hydrofluoric acid (the etching and polishing of glass) has not dwindled, but has been superseded by the requirements of other industries. Again, because of the high proportion of hydrogen fluoride used captively, it is hard to fix use patterns exactly. The estimates of Table 15, however, show relative amounts and show trends in use. The relative importance of various uses has not changed much since the late 1950s, though the production of fluorinated organic compounds rose greatly in total amount until the mid-1970s.

The largest use for hydrogen fluoride is in the manufacture of aluminum fluoride and cryolite (sodium aluminum fluoride) as the fused salt solvent for aluminum oxide in the electrolytic manufacture of aluminum (see Aluminum compounds). About 0.35 t of hydrogen fluoride are needed to make 1 t of aluminum. This use has increased less rapidly than the expansion of aluminum production because of greater efficiency in recycling fluorine values, and because of the production of some of the fluoride salts from silicon tetrafluoride by-product of the manufacture of phosphate fertilizers.

The principal fluorine-containing organic compounds are the chlorofluoromethanes used as refrigerants and formerly as pressurizing gases; some chlorofluoroethanes used as foaming agents and cleaning fluids; fluorine-containing ethylene and propylene to be converted to polymers; and longer-chain fluorocarbons converted to soil-resistant coatings for textiles and leather. On average, ca 0.35 g of hydrogen fluoride are needed to produce one gram of fluorocarbon.

For uranium processing, hydrogen fluoride is used to make uranium tetrafluoride and to make elemental fluorine to convert the tetrafluoride to uranium hexafluoride, which is used in the diffusion process for the separation of uranium isotopes. The product of the uranium refinery, U_3O_8, is reduced by hydrogen to UO_2. Treatment with hydrogen fluoride gives UF_4, and reaction with fluorine produces UF_6. Stoichiometrically, 1 t of U_3O_8 would require 0.43 t of hydrogen fluoride for the overall

Table 15. Distribution of Uses for Hydrogen Fluoride in the U.S., %

	1957	1962	1967	1972	1977
aluminum production					
aluminum fluoride			32	26	
cryolite	40	40	12	12	40
chlorofluorocarbons, including pressurizing gases, refrigerants, and polymers	28	34	37	40	37
uranium processing	12	11	2	2	7
petroleum alkylation	4	5	3	4	5
stainless steel pickling	5	3	3	4	4
other uses, including glass etching, other fluorides, sand castings, rocket propellant stabilizers, electronic circuits, sours and stain removers, oil-well acidizing, and mineral analysis	11	7	11	12	7

conversion. Considerable hydrogen fluoride passes through the hydrofluorination step with the water of reaction. This has been returned to the market as aqueous hydrofluoric acid.

In the petroleum industry, anhydrous hydrogen fluoride is a liquid catalyst for alkylation of aromatic hydrocarbons to produce octane improvers for gasoline. This use continues to be important: in 1978, U.S. refiners scheduled eight new HF alkylation plants with a total capacity of 7950 m^3 (50,000 barrels) of alkylate per day for early completion (57). Total U.S. HF alkylation capacity in 1978 was 56,870 m^3 (357,700 barrels) per day, and 1.26–3.14 kg of hydrogen fluoride were used per cubic meter of alkylate. Anhydrous hydrogen fluoride is also a catalyst for disproportionation, isomerization, polymerization, and dehydration reactions.

The application of hydrofluoric acid to the removal of scale from stainless steels has increased somewhat more slowly than U.S. production of these steels, because of increasing imports. Glass etching, as for the inner surfaces of light bulbs, requires aqueous hydrofluoric acid. Hydrofluoric acid, to which ammonium fluoride is added, etches to a polished surface for the final treatment of cut glass. Other uses include preparation of fluorides other than aluminum; removal of sand from metal castings; reduction of the corrosiveness of nitric acid rocket propellant oxidizers; preparation of microelectronic circuits; laundry sours and stain removers; oil well acidizing; and mineral analysis.

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