

Table of Contents

Page

Compounds of Fluorine	1
1 Compounds of Fluorine with Noble Gases	1
2 Compounds of Fluorine with Hydrogen	1
2.1 Hydrogen Fluoride	1
2.1.1 Preparation. Handling. Uses	1
Laboratory Preparation, Dehydration, and Purification	1
Preparation	1
Dehydration. Determination of Traces of H_2O	2
Purification on the Laboratory Scale	4
Industrial Production	5
General Remarks	5
Manufacture from CaF_2	6
Manufacture from CaF_2 and H_2SO_4	6
General Remarks	6
Industrial Processes	7
Modified Processes	8
Manufacture from CaF_2 without the Use of H_2SO_4	10
Manufacture from H_2SiF_6	10
General Remarks	10
Manufacture from H_2SiF_6 and H_2SO_4	11
Manufacture via NH_4F or NH_4HF_2	11
Manufacture by Other H_2SiF_6 Processes	13
Industrial Purification and Dehydration	16
Preparation of $H^{18}F$	18
Preparation of DF and of TF	18
Thermodynamic Data of Formation	19
Handling. Storage. Transport	20
Materials	20
Storage. Transport	21
Uses	22
Toxicity, Protection	23
2.1.2 Molecules	24
The Molecule HF (and DF, TF)	24
Electron Configuration. Term Values	24
Ionization Potentials. Photoelectron Spectra.	
Photoionization Ion-Yield Curves. (e,2e) Spectra	27
HF Molecule	27
DF Molecule	28
Proton Affinity	30
Polarizability	31
Dipole Moment. Dipole Moment Function	31
Quadrupole Moment. Octupole Moment. Hexadecapole Moment	34
Quadrupole Coupling Constant	35

	Page
Magnetic Constants. Molecular-Beam Resonance.	
Nuclear Magnetic Resonance	35
Rotational and Vibrational Constants. Internuclear Distance	38
Potential Energy Functions	44
Dissociation Energy	46
Quantum Chemical Calculations	47
Introduction	47
Tables on ab initio Calculations	50
Semiempirical Calculations	69
The Dimeric Molecule (HF) ₂	72
Molecular Properties and Spectra	72
Quantum Chemical Calculations	74
Bibliography of Nonempirical and Semiempirical Calculations for (HF) ₂	74
Polymeric Molecules (HF) _n	79
Molecular Properties and Spectra	79
Quantum Chemical Calculations	80
2.1.3 Constitution of Gaseous and of Liquid Phase	82
Gaseous Phase	82
Liquid Phase	87
2.1.4 Crystal Structure. Lattice Vibrations. Electronic Band Structure	88
2.1.5 Mechanical and Thermal Properties	92
Density. pVT Data. Vapor Pressure	92
Sound Velocity. Compressibility	94
Equation of State	94
Melting Curve. Triple Point Temperature. Cryoscopic Constant	95
Normal Boiling Point. Critical Constants	95
Heat of Vaporization	95
Heat Capacities. Thermodynamic Functions	96
Viscosity. Self-Diffusion. Thermal Conductivity	99
2.1.6 Electrical Properties	100
2.1.7 Optical Properties and Spectra	101
Refractive Index	102
Rotational Spectra	102
Microwave Absorption. Raman Effect. Far IR Absorption and Emission. Superradiance	102
Vibrational-Rotational Spectra	106
Raman Effect	106
IR Absorption	107
Gaseous HF	107
General	107
Line Positions. Line Shifts	108
Line and Band Strengths. Matrix Elements. Line Shapes	110
Perturbations of Vibrational-Rotational Lines by Foreign Gases	112
HF in Liquid Solutions	114
Matrix-Isolated HF. Crystalline HF	115

	Page
Spontaneous Emission in the Visible and IR	116
Electronic Spectra. UV Absorption and Emission	118
2.1.8 HF and DF Chemical Laser	120
General Remarks	120
Laser Processes	122
Pulsed HF and DF Lasers	124
Continuous-Wave (cw) HF and DF Lasers	126
Types of Reaction in HF and DF Chemical Lasers	128
General Remarks. Three-Atom Exchange Reactions	128
General Remarks	128
Three-Atom Exchange Reactions	129
Abstraction Reactions	136
Elimination Reactions	141
Radical Combination Reactions	141
Insertion Reactions	142
Addition Reactions	142
Photoelimination Reactions	143
Mercury-Sensitized Elimination Reactions	144
Laser Lines	145
2.1.9 DF-CO ₂ Transfer Chemical Laser	148
2.1.10 Energy-Transfer Processes	150
Vibrational Energy Transfer	150
HF Self-Deactivation	151
DF Self-Deactivation	153
Deactivation of HF by DF and of DF by HF	155
Deactivation by Species Other than HF, DF	155
Rotational Energy Transfer	165
2.1.11 Chemical Reactions	167
General Remarks	167
Isotope Exchange Reactions	167
Reactions of Gaseous Hydrogen Fluoride	168
Dissociation of HF	168
Reactions with Elements	170
Reactions with Hydrogen	170
With Hydrogen Atoms	170
With the Hydride Ion	171
With Hydrogen Molecules	172
Reactions with Oxygen	172
Reactions with Halogens	172
With Fluorine Atoms and Molecules	172
With Chlorine, Bromine, and Iodine Atoms	172
Reactions with Carbon	172
Reactions with Silicon	173
Reactions with Alkali Metals	173
Reactions with Alkaline Earth Metals	173
Reactions with Other Metals	174

	Page
Reactions with Inorganic Compounds	176
Reactions with Compounds of Nonmetals	176
Reactions with Compounds of Metals	178
Solubilities and Reactions in Liquid Anhydrous Hydrogen Fluoride	181
General Remarks	182
Autoprotolysis of HF	182
Acidity of HF	183
Solubilities and Reactions of Elements	184
Solubilities and Reactions of Inorganic Compounds	186
Noble Gas Fluorides	186
Nitrogen Compounds	187
Chlorine Compounds	190
Bromine Compounds	192
Iodine Compounds	193
Sulfur, Selenium, and Tellurium Compounds	194
Boron Compounds	196
Hydrogen Cyanide	199
Silicon Tetrafluoride	199
Phosphorus Compounds	199
Arsenic Compounds	200
Antimony Compounds	202
Bismuth Fluorides	205
Alkali Fluorides. Ammonium Fluorides	205
Group II Metal Fluorides	210
Aluminium, Indium, and Thallium Fluorides	211
Cerium and Praseodymium Fluorides	212
Titanium, Zirconium, and Thorium Fluorides	212
Germanium, Tin, and Lead Fluorides	213
Vanadium, Niobium, and Tantalum Fluorides	214
Chromium, Molybdenum, Tungsten, Uranium, and Plutonium Fluorides and Oxide Fluorides	216
Manganese and Technetium Fluorides. Rhenium Fluorides and Oxide Fluorides	217
Iron, Cobalt, and Nickel Fluorides	218
Copper, Silver, and Gold Compounds	219
Platinum-Group Metal Compounds	221
Electrochemical Procedures in Liquid HF	222
Electrode Materials	222
Polarography	223
Reference Electrodes	224
Reactions of Anhydrous HF with Organic Compounds. Solubility	225
General Remarks	225
Solubilities. Thermodynamic Data	226
Acid-Base Reactions	228
Alcohols	228
Ethers	229
Ketones	229
Carboxylic Acids	229
Nitrogen Compounds	230

	Page
Sulfur Compounds	231
Aromatic Hydrocarbons	231
Intermolecular Complexes of HF	232
2.1.12 The HF-H ₂ O System	238
Phase Diagram	238
Complexes of HF with H ₂ O	241
The Gaseous H ₂ O...HF Complex	241
Higher Gaseous Complexes of HF with H ₂ O	243
Solid Complexes of HF and H ₂ O	245
2.1.13 The Aqueous Solution (Hydrofluoric Acid)	246
Absorption of Gaseous HF by Water and by Aqueous Solutions	246
Enthalpy Data for Dissolution of Gaseous and Liquid HF in Water and in Aqueous HCl	247
Definitions	247
The Enthalpy of Solution and Dilution	248
Enthalpy and Gibbs Free Energy of Solution at Infinite Dilution	249
Enthalpy and Gibbs Free Energy of Formation of Aqueous HF at Finite and Infinite Dilution	250
Enthalpy of Formation of HF Dissolved in Hydrochloric Acid	251
The Nature of the Aqueous Solution	253
Survey	253
Dissociation and Association Constants and Quotients	255
Dissociation and Association Constants	255
Dissociation Quotient, Association Quotient, and Overall Stability Quotient at the Finite Ionic Strength I	257
K _{1,1} , K _{1,2} , $\beta_{1,1}$, $\beta_{1,2}$, and $\beta_{2,2}$ as a Function of Temperature	259
K _{1,1} and K _{1,2} in D ₂ O	260
K _{1,1} in Supercritical Water	261
Dimerization Constant	261
Ionization Constant of H ₂ O in HF	262
Thermodynamic Parameters for the Dissociation of HF and for the Association Reactions Giving HF ₂ ⁻	262
Activities and Concentrations of Species in Aqueous Solution	265
Acidity of Hydrofluoric Acid	267
pH Values, Acidity Functions	267
Acidity Functions	268
Thermodynamic Explanation of the Strength of Aqueous HF	269
The R ₀ (F) Function	270
Thermodynamic Data and Hammett Function H ₀ of HF for Mixtures of Water and Organic Compounds	271
Mechanical and Thermal Properties	273
Density	273
Heat Capacity	274
Enthalpy, Entropy	275
Surface Tension, Viscosity	276
IR and Raman Spectra	276
Nuclear Magnetic Resonance	278
Relaxation Rates and Related Data	278
Chemical Shifts in Aqueous Solutions	279

	Page
Electrochemical Behavior	283
Metal Ion/Metal Couples in Aqueous HF	283
Conductance	283
Electrolysis	287
Electroanalytical Methods Using Aqueous HF as the Supporting Electrolyte	287
Chemical Reactions	288
Isotope-Exchange Reactions	288
Reaction with Positrons	289
Reactions with Elements	289
Reactions with Nonmetals	289
Reactions with Metals	289
Reactions with Oxides	292
Reactions with Oxides of Nonmetals	292
Reactions with Metal Oxides	294
Reactions with Fluorides	296
Reactions with Fluorides of Nonmetals	296
Reactions with Metal Fluorides	296
Reactions with Acids	298
2.1.14 The F^- Ion	299
Solvation	299
Introduction	299
Thermodynamic Properties	302
Dielectric, Mechanical, and Transport Properties	307
Spectroscopic Properties	309
Gas-Phase Reactions	313
Reactions with H_2O	313
Reactions with SO_2 , NH_3 , and CO_2	315
Complex Formation with Fluoride Ions	315
Ion Exchange	316
2.2 The Ions HF^+ and DF^+	317
2.3 The Ion HF^-	322
2.4 The Molecule H_2F and the Ions H_2F^+ and H_2F^-	324
2.4.1 The Molecule H_2F	324
2.4.2 The Ion H_2F^+	325
2.4.3 The Ion H_2F^-	328
2.5 The Ion $H_3F_2^+$	328
2.6 The Molecule HF_2 and the Ion HF_2^-	329
2.6.1 The Molecule HF_2	329

	Page
2.6.2 The Ion HF_2^-	329
General Remarks	329
Structure, Point Group	330
Internuclear Distances	330
^1H and ^{19}F NMR	331
Molecular Vibrations, Potential Functions	333
Hydrogen Bond Energy	335
Quantum Chemical Calculations	337
2.7 The Ions H_2F_3^-, H_3F_4^-, and H_4F_5^-	340
2.8 Additional F- and H-Containing Species	342
Table of Conversion Factors	344

Compounds of Fluorine

1 Compounds of Fluorine with Noble Gases

Compounds of fluorine with noble gases are covered in "Edelgasverbindungen" Erg.-Werk, Bd. 1, 1970.

2 Compounds of Fluorine with Hydrogen

2.1 Hydrogen Fluoride HF (and its isotopic species)

2.1.1 Preparation. Handling. Uses

For formation of HF see the chapter on the gas-phase reactions of fluorine with hydrogen in "Fluorine" Suppl. Vol. 2, 1980, as well as Chapter 2.1.8 in this volume. For formation of hydrofluoric acid see also p. 246.

General References:

W. Augustyn, J. Chmiel, M. Grobelny, Fluorine and Its Inorganic Compounds, Technology and Application, Chemik [Gliwice] **12** [1959] 53/7.

Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd Ed., Vol. 10, New York - Chichester - Brisbane - Toronto 1980, pp. 733/53.

H. R. Leech, Some Aspects of Inorganic Fluorine Compounds in Chemical Industry, Chem. Ind. [London] **1960** 242/50.

A. Level, Industrial Fluorine Chemistry, Chim. Ind. Genie Chim. **102** [1969] 1077/82.

T. A. O'Donnell, Fluorine in: J. C. Bailar, H. J. Emeléus, R. Nyholm, A. F. Trotman-Dickenson, Comprehensive Inorganic Chemistry, Vol. 2, Oxford 1973, pp. 1009/106.

A. S. Rudge, The Manufacture and Use of Fluorine and Its Compounds, London - New York - Toronto 1962.

Ullmanns Encyklopädie der technischen Chemie, 4th Ed., Vol. 11, Weinheim/Bergstr. 1976, pp. 595/602.

2.1.1.1 Laboratory Preparation, Dehydration, and Purification

2.1.1.1.1 Preparation

The laboratory preparation of HF is rarely undertaken because HF is available in generally sufficient purity from commercial sources (see p. 5). Procedures for preparing high-purity HF from commercial HF are given below.

Anhydrous HF can be prepared by thermal decomposition of dry KHF_2 at 500°C in a noble metal apparatus followed by distillation of the hydrogen fluoride [1], see also "Fluor" Erg.-Bd. 1, 1959, p. 144. It is important to use dried KHF_2 if low-conductivity, i.e., water-free, HF is required. The salt is dried by electrolytic methods [2], by heating in fluorine at 150°C [1], or by heating in vacuo up to 200°C for ten hours or more [3].

Instead of the potassium salt, the nonhygroscopic and thermally less stable sodium salt, NaHF_2 , can be used as the source of HF [4]. The hydrogen fluoride formed by decomposition of NaHF_2 (15 min at 350°C , final temperature 450°C) was fractionated in a fluorothene distillation assembly to give samples with electrical conductivities as low as $1.6 \times 10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$ [4], see also [5].

A generator for use in HF adsorption studies based on the temperature-dependent dissociation of NaHF_2 is described in [6]. NaHF_2 gives HF pressures of 0.001 to 0.3 Torr at 60 to 135°C . This generator allows a dry carrier gas (N_2) to pass through the thermoregulated chamber filled with crystalline NaHF_2 to yield HF concentrations of 5 to 1000 ppm at flow rates ≤ 5 L/min for periods up to one year [6].

References:

- [1] W. Kwasnik (in: G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, Stuttgart 1975, pp. 164/6). – [2] J. H. Simons (J. Am. Chem. Soc. **46** [1924] 2179/83; Chem. Rev. **8** [1931] 213/35; Inorg. Syn. **1** [1939] 134/6). – [3] M. Kilpatrick, F. E. Luborsky (J. Am. Chem. Soc. **75** [1953] 577/84). – [4] M. E. Runner, G. Balog, M. Kilpatrick (J. Am. Chem. Soc. **78** [1956] 5183/6). – [5] R. L. Jarry, W. Davis (J. Phys. Chem. **57** [1953] 600/4).
[6] F. M. Kimmerle, A. Archambault, G. Dube (Can. J. Chem. **56** [1978] 2034/8).

2.1.1.1.2 Dehydration. Determination of Traces of H_2O

A great number of methods have been proposed in recent years for the dehydration of HF. The best seems to be the addition of SOCl_2 [1, 2, 3] since the reaction products (SOF_2 , HCl , and SO_2) are all gases and can be easily removed. An additional distillation is also useful.

The treatment of hydrogen fluoride containing small amounts of water with desiccants such as CoF_3 [4, 5], CoF_3 and NaF [6], VF_5 [3], and ClF_3 [3] has been recommended. The opinions on the usefulness of elemental fluorine as a desiccant differ. According to [7] hydrogen fluoride used in conductance work can be dried by elemental fluorine. Kwasnik [2] recommends introduction over 30 min directly into the cooled HF product. On the other hand, attempts to prepare anhydrous hydrogen fluoride by bubbling fluorine through the acid [3] were reported to be unsuccessful.

The procedure of continuously drying hydrogen fluoride by electrolysis has been suggested several times [8, 9, 10]. The addition of other electrolytes, usually KF , enables the electrolysis to be continued until the water content has been reduced even further. However, the rates of discharge of O_2 and OF_2 are much lower than the rate of discharge of fluorine, and thus large quantities of fluorine must be released before dry HF is obtained [11]. The current reversal technique [12] leads to more effective drying on account of extensive anodic depolarization. A further advantage is that the high average current reduces the time required for drying and thus markedly reduces the attack on the Ni electrode [12]. Also see the chapter on purification on p. 4.

The water content in HF is determined by titration using the Karl Fischer reagent [13] and by conductance measurements. The direct determination of H_2O in the acid by titration is based on the reaction $\text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O} = 2\text{HI} + \text{H}_2\text{SO}_4$. Anhydrous- CH_3OH and pyridine are used for the solvation of iodine and SO_2 . The methods used for the fixation of the hydrogen fluoride vary; for example, cyclohexene and KHF_2 [14] have been used for

this purpose. Aqueous HF can be titrated directly, see [15]. The determination of traces of water in hydrogen fluoride by the Karl Fischer reagent is described in [16].

Since the titration does not give the required accuracy over the range from zero to a few tenths of a percent of H_2O [17], many attempts have been made to determine the H_2O content in HF on the basis of the electrical conductivity, for example [18, 19]. The conductivity of liquid hydrogen fluoride is changed to almost the same extent by moisture and H_2SO_4 . The presence of other impurities has no appreciable effect on the electrical conductivity [17]. For extremely pure hydrogen fluoride a limiting value of the electrical conductivity of $1.0 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ is assumed, see p. 101. The investigations made by Wejnar [20] show the effect of SO_2 on the conductivity of wet HF (up to 1.5% H_2O) in continuous HF production [20]. Conductivity measurements give the relation between the H_2O content a (in wt%) of hydrogen fluoride and the specific resistance R (in $\Omega \cdot \text{cm}$) at -15°C [7]: $\log a = 1.808 - 1.528 \log R_{-15}$. The effect of temperature on R is represented by $R_t = R_{-15} \cdot (0.9307 - 4.02 \times 10^{-3}t + 1.01 \times 10^{-4}t^2)$ for $t = -50$ to $+10^\circ\text{C}$ [7], see also [11].

There are few reliable measurements of the conductivity of H_2O in HF. Engelbrecht and Nachbaur [21] studied the system H_2O -HF between 20 to 90% HF at 0°C , and Fredenhagen, Cadenbach [22] have investigated this system at -15°C . The results obtained by [22] are in good agreement with the values calculated by [11, pp. 213/4] from the equations (given above) of [7]. More information is given in Chapter 2.1.13.7.

References:

- [1] K. Wiechert (Z. Anorg. Allgem. Chem. **261** [1950] 310/23, 313/5). – [2] W. Kwasnik (in: G. Brauer, Handbuch der Präparativen Anorganischen Chemie, Stuttgart 1975, p. 165). – [3] N. S. Nikolaev, Yu. A. Buslaev, S. V. Vlasov (Zh. Neorgan. Khim. **7** [1962] 945/6; Russ. J. Inorg. Chem. **7** [1962] 488/9). – [4] M. T. Rogers, J. L. Speirs, M. B. Panish, H. B. Thompson (J. Am. Chem. Soc. **78** [1956] 936/8). – [5] H. H. Hyman, M. Kilpatrick, J. J. Katz (J. Am. Chem. Soc. **79** [1957] 3668/71).
- [6] R. L. Jarry, W. Davis (J. Phys. Chem. **57** [1953] 600/4). – [7] R. Ukazi, I. Kageyama (Bunseki Kagaku **9** [1960] 604/8 from C. A. **56** [1962] 9419). – [8] J. H. Simons et al. (Trans. Electrochem. Soc. **95** [1949] 47/68). – [9] S. Kongpricha, A. F. Clifford (J. Inorg. Nucl. Chem. **18** [1961] 270/5). – [10] J. Burdon, J. C. Tatlow (Advan. Fluorine Chem. **1** [1960] 129/98, 132/7, 160/3).
- [11] M. F. A. Dove, A. F. Clifford (Chem. Nichtwässrigen Ionis. Lösungsm. **1** [1971] 123, 213/4). – [12] H. H. Rogers, S. Evans, J. H. Johnson (J. Electrochem. Soc. **111** [1964] 701/4). – [13] K. Fischer (Angew. Chem. **48** [1935] 394/6). – [14] N. S. Nikolaev, I. F. Alenchikova (Zavodsk. Lab. **24** [1958] 418/9; Ind. Lab. [USSR] **24** [1958] 472/4). – [15] J. Mitchell, D. M. Smith (Aquametry, Interscience, New York - London 1948, p. 243).
- [16] Phillips Petroleum Co. (Hydrofluoric Acid Alkylation, Bartlesville, Okla., 1946 from J. Mitchell, D. M. Smith, Aquametry, Interscience, New York - London 1948, pp. 243/5). – [17] S. V. Usikov, L. K. Vasil'eva (Zh. Fiz. Khim. **39** [1965] 2394/5; Russ. J. Phys. Chem. **39** [1965] 1278/9). – [18] M. Kilpatrick, F. F. Luborsky (J. Am. Chem. Soc. **75** [1953] 577/84). – [19] M. E. Runner, G. Balog, M. Kilpatrick (J. Am. Chem. Soc. **78** [1956] 5183/6). – [20] H. Wejnar (Chem. Prumysl **11** [1961] 303/5).
- [21] A. Engelbrecht, E. Nachbaur (Monatsh. Chem. **90** [1959] 367/70). – [22] K. Fredenhagen, G. Cadenbach (Z. Physik. Chem. **146** [1930] 245/80, 257).

2.1.1.1.3 Purification on the Laboratory Scale

The methods employed in purifying commercial grade HF are distillation (fractional, repeated, isothermal, and sub-boiling distillation) and filtering. The aim is to remove very small amounts of Si, As, Sb, Fe, heavy metals, organic matter, etc. from commercial grade HF to yield high-purity HF. (The dehydration is described separately on p. 2.)

In earlier distillation work, container materials used were platinum, silver, copper, and sometimes quartz. Nowadays, these materials have been replaced by plastics, such as polyvinyl chloride, polyethylene, and teflon (see also p. 20). The distillation rates are frequently very low (centiliters per day to centiliters per hour) and differ from method to method. Some additives are included in the various processes: BaCO_3 or Ba(OH)_2 (to remove SO_2 and H_2SO_4) [1], Ag_2CO_3 (to remove Cl^-) [1], H_2O_2 and Ba(OH)_2 [2], KMnO_4 and mannitol [3, 4] (for oxidizing and complexing metal impurities), and NaF (for H_2SiF_6 removal) [5].

Filtering. Tilton et al. [6] describe a method which consists of passing gaseous HF through a filter of fine teflon shavings and a teflon bubbler into triple-distilled H_2O in an ice-cooled platinum vessel [6]. A polyethylene apparatus in which HF gas is carried in N_2 through polyethylene beads and a solution of NaF (to remove H_2SiF_6) and then into H_2O distilled in a polyethylene still is described in [5]. The resulting 50% acid contains $> 1\mu\text{g}$ Cu, $> 1\mu\text{g}$ Fe, and $5\mu\text{g}$ Si per mL acid [5]. Ultrapure 50% hydrofluoric acid containing 2 ppb/mL K and 0.08 ppb/mL Pb needed in analytical work (returned lunar samples) was produced by [7]. HF gas passes a teflon filter and is then frozen by cooling with liquid N_2 . After distillation the gas is introduced into very pure H_2O [7]. Gaseous HF is also purified by passing through an active-carbon filter [4] or a fine filter made of polychloroethylene [3]. After absorption in H_2O (specific resistance 10×10^6 to $15 \times 10^6 \Omega \cdot \text{cm}$ [3]) the aqueous HF is distilled. Treatment with mannitol and KMnO_4 [3, 4] is also included in this method.

Fractionation. The distillation columns described in [8] and [9] are similar. They are suitable for fractionation of commercial grade hydrogen fluoride to obtain an anhydrous product. The distillate is taken off in the liquid phase from the vicinity where the Pt condenser is cooled to -40°C to yield some 120 mL/day. The conductivity of the product was on the order of $10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$ at 25°C [9].

Repeated Distillation. Very pure hydrogen fluoride (e.g., $< 1\mu\text{g}$ Pb/g) is obtained by distilling 100% HF at room temperature from a feed bottle into a dry-ice cooled collection bottle five times (polyethylene still, total distillation time of 10 h). The advantage of this method is the preparation of pure HF solutions of any desired strength by carefully mixing the hydrogen fluoride with high-purity triple-distilled H_2O [10].

Isothermal Distillation. This method developed by [13] and used by [2, 11, 12] is simply the molecular diffusion of gaseous HF from commercial HF into deionized H_2O at constant temperature, usually 18 to 25°C . Polyvinyl chloride [2] and polyethylene [11, 12] stills are suitable. Disadvantages: length of the procedure on account of the low transfer rates and the quality of the acid obtained, which depends on the quality of the H_2O used for absorption. Advantage: simple room-temperature method.

Sub-boiling Distillation. This method [14] involves a slow sub-boiling evaporation at temperatures (70 to 85°C [14]) well below the boiling point of the azeotropic mixture $\text{HF}/\text{H}_2\text{O}$ (111.4°C , see p. 240). This method was improved in [15, 16]. The feed acid used was 48% [14 to 16]. Stills were made of polyethylene [14] and teflon [15, 16]. Disadvantage of this method: only up to 48% hydrofluoric acid can be obtained.

The effectiveness of a distillation of hydrofluoric acid (48%) as analyzed by spectrographic methods [17] is shown in the following table (values in ppb) [16]:

element	feed	product	residue	element	feed	product	residue
Al	7	2	20	Mg	20	3	30
B	2	<0.5	3	Mn	3	0.2	5
Ca	700	300	200	Ni	5	<1	20
Cr	3	<1	30	K	20	<5	30
Co	3	<1	7	Na	>1000	50	>1000
Cu	30	2	80	Sr	<10	<10	<10
Fe	30	2	100	Zn	50	<1	200
Pb	2	<1	2				

References:

- [1] A. Ostaszynski, Z. Piasek (Bull. Acad. Polon. Sci. **5** [1957] 523/6 from C. A. **1958** 948).
 – [2] R. Osicki (Przemysl Chem. **42** [1963] 32/3). – [3] M. I. Kafyrov, A. V. Yuzo, A. A. Fakeev et al. (Fr. 1596497 [1968/70]; C. A. **74** [1971] No. 101216). – [4] I. I. Angelov, V. S. Nechaeva, A. A. Fakeeva, Z. V. Ivanov, L. A. Sazikova (Tr. Vses. Nauchn. Issled. Inst. Khim. Reaktivov Osobo Chist. Khim. Veshchestv **33** [1971] 285/92 from C. A. **78** [1973] No. 23343). – [5] H. Stegemann (Z. Anal. Chem. **154** [1957] 267/9).
 [6] G. R. Tilton, C. Patterson, H. Brown et al. (Bull. Geol. Soc. Am. **66** [1955] 1131/48, 1135). – [7] M. Tatsumoto (Anal. Chem. **41** [1969] 2088/9). – [8] M. E. Runner, G. Balog, M. Kilpatrick (J. Am. Chem. Soc. **78** [1956] 5183/6). – [9] J. Shamir, A. Netzer (J. Sci. Instr. **2** [1968] 770/1). – [10] M. S. Lancet, I. M. Huey (Anal. Chem. **46** [1974] 1360/1).
 [11] W. Kwestrov, I. Visser (Analyst **90** [1965] 297/8). – [12] J. Marecek, J. Ditz (Chem. Listy **59** [1965] 972/8). – [13] H. Irving, I. I. Cox (Analyst **83** [1958] 526/8). – [14] P. P. Coppola, R. C. Hughes (Anal. Chem. **24** [1952] 768). – [15] J. M. Mattinson (Anal. Chem. **44** [1972] 1715/6).
 [16] K. Little, J. D. Brooks (Anal. Chem. **46** [1974] 1343/5). – [17] N. A. Kershner, E. F. Joy, A. J. Barnard (Appl. Spectrosc. **25** [1971] 542/9).

2.1.1.2 Industrial Production

2.1.1.2.1 General Remarks

In the last 30 years the industrial production of nitrogen fluoride and hydrofluoric acid has increased considerably since HF is the most important starting material for fluorine chemistry (see Chapter 2.1.1.7, p. 22, on uses of HF). The consumption of HF in the western hemisphere has been reported as [1]:

1964	1970	1972	1980
555 000 t	960 000 t	1 045 000 t	1 820 000 t (estimated)

The total HF consumption in the USA increased from 205 000 t in 1965 to 316 000 t in 1979 [2], see also [3, 4].

A large number of publications, usually patents, are available on industrial production of HF. Selected publications are summarized in the following chapters to survey new developments.

References:

[1] W. Schabacher (in: Ullmanns Encyclopädie der technischen Chemie, 4th Ed., Vol. 11, Weinheim/Bergstr. 1976, p. 595). – [2] F. Lombardo (J. Fluorine Chem. **18** [1981] 1/24, 4). – [3] J. F. Gall (Kirk-Othmer Encycl. Chem. Technol. 3rd Ed. **10** [1980] 733/52, 747/9). – [4] J. Massonne (Chemiker-Ztg. **96** [1972] 65/75).

2.1.1.2.2 Manufacture from CaF_2 **2.1.1.2.2.1 Manufacture from CaF_2 and H_2SO_4** **2.1.1.2.2.1.1 General Remarks**

Hydrogen fluoride is almost always obtained by reacting acid-grade fluorspar (CaF_2) with H_2SO_4 : $\text{CaF}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{HF} + \text{CaSO}_4$. This well-known process was described in "Fluor" Erg.-Bd. 1, 1959, p. 146. Acid-grade fluorspar is obtained as finely ground flotation product from crude fluorspar (CaF_2 content 50 to 90%) or as a synthetic product from H_2SiF_6 (see p. 15). Generally it has the following specifications:

CaF_2	min. 97%	$\approx 98\%$	min. 96.5 to 98%
SiO_2	max. 1%	max. 1%	max. 1%
S	max. 0.01%	max. 0.03%	0.05%
CaCO_3	—	max. 1%	principal impurity
moisture	—	max. 1%	max. 0.05%
flotation agent	0.03%	—	—
Ref.	[1]	[2]	[3]

The dried flotation spar is reacted with ca. 98% sulfuric acid (possibly with 20 or 65% oleum added) or with SO_3 and steam (see p. 7) [1]. Contamination of the fluorspar causes such side reactions as [1, 3, 4]: $\text{SiO}_2 + 2\text{CaF}_2 + 2\text{H}_2\text{SO}_4 \rightarrow \text{SiF}_4 + 2\text{CaSO}_4 + 2\text{H}_2\text{O}$; $\text{SiO}_2 + 4\text{HF} \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O}$; $\text{SiF}_4 + 2\text{HF} \rightarrow \text{H}_2\text{SiF}_6$; $\text{CaCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O} + \text{CO}_2$; $2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S} + 2\text{H}_2\text{O}$; $\text{H}_2\text{SO}_4 + \text{H}_2\text{S} \rightarrow \text{S} + \text{SO}_2 + 2\text{H}_2\text{O}$; $\text{R}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 \rightarrow \text{R}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O}$, where R = Fe, Al. These reactions lower the yield of HF and produce unwanted impurities [1, 3, 4].

The conversion of CaF_2 into HF is carried out in a heated rotating kiln made of low-silicon steel. The purity of the HF obtained is affected by the purity and fineness of the fluorspar, the concentration of the H_2SO_4 , the ratio $\text{CaF}_2/\text{H}_2\text{SO}_4$ (determined usually to assure the quality of the by-product CaSO_4), the temperature of the reaction, and the mixing efficiency [4], see also [1 to 3].

References:

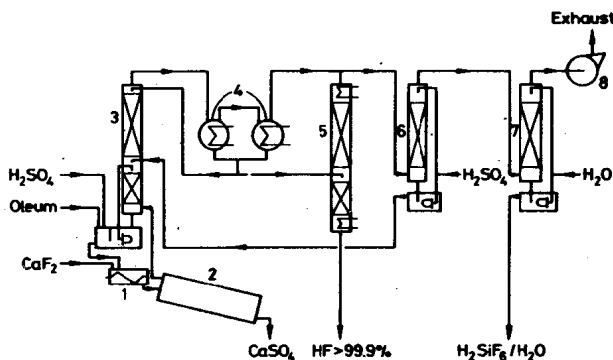
[1] W. Schabacher (in: Ullmanns Encyclopädie der technischen Chemie, 4th Ed., Vol. 11, Weinheim/Bergstr. 1976, pp. 598/606). – [2] W. R. Rogers, K. Müller (Chem. Eng. Progr. **59** No. 5 [1963] 85/8). – [3] D. Candido, G. P. Mathur (Ind. Eng. Chem. Process Design Develop. **13** [1974] 20/6; C.A. **80** [1974] No. 52699). – [4] J. F. Gall (Kirk-Othmer Encycl. Chem. Technol. 3rd Ed. **10** [1980] 733/52, 742/4).

2.1.1.2.2.1.2 Industrial Processes

This chapter gives some examples for the manufacture of hydrogen fluoride in continuous operations. For processes developed before the middle fifties, see "Fluor" Erg.-Bd. 1, 1959, p. 156.

The Buss AG (Switzerland) [1 to 4] developed a process which has been used all over the world [5]. A flow sheet for this process is shown in Fig. 1 from [5]. Corrosion of the externally heated rotating kiln is considerably reduced by a special Ko-kneader [1 to 4], a continuous screw conveyor of corrosion-resistant alloy, before the kiln. About 30% of the mixture of CaF_2 and preheated H_2SO_4 react at 100 to 120°C in the Ko-kneader. The dust, water, and sulfur content of the crude gas is retained in the pre-wash system. Oleum in the column sump binds the used wash water. The pre-purified gas is liquefied in two condensers to form low-moisture, pre-purified HF, which can be further purified by distillation to ca. 99.9% HF [6].

Fig. 1



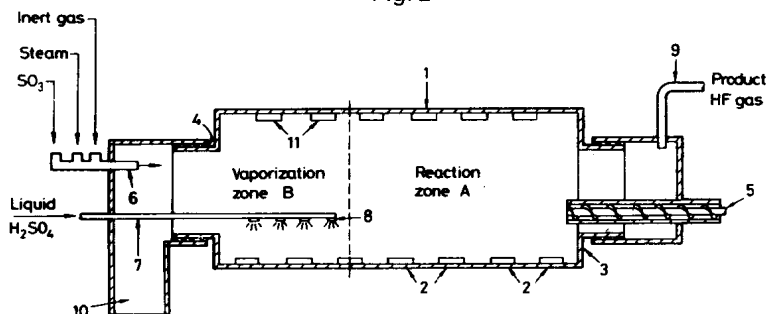
Manufacture of hydrogen fluoride, Buss AG (Switzerland) [5].

- 1) Ko-kneader. – 2) Rotary kiln. – 3) Pre-wash system. –
- 4) Condensers. – 5) Distillation column. –
- 6) H_2SO_4 absorption tower. – 7) H_2O absorption tower. –
- 8) Exhaust.

The corrosion of the rotary kiln can be also reduced by an Allied Chemical Corp. process [7], in which a part of the CaSO_4 formed in the center of the reaction zone is recycled by an internal screw conveyor to the end of the rotating kiln.

A Du Pont process [8 to 10] uses a continuous countercurrent reactor with heat generated internally from the reaction of SO_3 and steam, as shown in Fig. 2, p. 8. The interior of the reactor is divided into a reaction zone and a vaporization zone. The CaF_2 is fed continuously into the reactor by the screw conveyor. Steam and SO_3 vapor (effectively ≈ 98 to 99% H_2SO_4) enters the reactor in the vaporization zone. Liquid 98 to 100% H_2SO_4 vaporizes in the vaporization zone as it is sprayed through nozzles. The amount of H_2SO_4 is approximately stoichiometric or 1 to 5% in excess. The temperature within the reaction zone is held between 150 to 300°C and does not exceed 335°C. HF gas containing small amounts of SiF_4 , CO_2 , SO_2 , H_2SO_4 vapor, and dust passes through a recovery train which isolates commercial grade HF ($\approx 98\%$ pure) by condensation and subsequent distillation [8 to 10].

Fig. 2



Manufacture of hydrogen fluoride, Du Pont (U.S.A.) [5, 6].

- 1) Rotating shell. — 2) Lifter blades. — 3), 4) Seals. — 5) Screw conveyor.
 — 6) Gas input (SO_3 , steam, inert gas). — 7) H_2SO_4 input. — 8) H_2SO_4 spraying by nozzles. — 9) HF output. — 10) CaSO_4 discharge.

References:

- [1] H. List, Buss AG (Swiss 319931 [1957] from C.A. **1957** 18503). — [2] H. List, R. Wollak, Buss AG (U.S. 2932557 [1960] from C.A. **1960** 21673). — [3] W. R. Rogers, K. Muller (Chem. Eng. Progr. **59** No. 5 [1963] 85/8). — [4] N. P. Chohey (Chem. Eng. **9** [1962] 94/6). — [5] J. Massonne (Chemiker-Ztg. **96** [1972] 65/75).
 [6] W. Schabacher (in: Ullmanns Encyklopädie der technischen Chemie, 4th Ed., Vol. 11, Weinheim/Bergstr. 1976, pp. 598/606). — [7] W. E. Watson, R. P. Troeger, Allied Chemical Corp. (U.S. 3607121 [1969/71] from C.A. **76** [1972] No. 5423). — [8] D. McMillan, C. C. Quarles, DuPont de Nemours (U.S. 3102787 [1960/66] from C.A. **60** [1964] 220). — [9] C. C. Quarles, DuPont de Nemours (U.S. 3278265 [1965/66] from C.A. **65** [1966] 19742). — [10] C. C. Quarles, DuPont de Nemours (U.S. 3282644 [1965/66]).

2.1.1.2.2.1.3 Modified Processes

Some patents describe modified procedures. A sintering apparatus is fed with a 1:1 ratio of CaF_2 and concentrated H_2SO_4 together with anhydrous CaSO_4 in 50 to 150% excess of the amount produced by the reaction. The temperature is held below 50°C , preferably at 15 to 20°C [1], see also [2 to 4].

Some patents describe processes in which HF or a similar substance is also added. For example, if the reaction between CaF_2 and H_2SO_4 is conducted in liquid HF and the system is kept fluid, heat transfer is improved [5]. A process which involves the formation of a mobile slurry of finely divided fluorspar (99% CaF_2) and H_2SO_4 containing HF (10 wt%) or FSO_3H at 10 to 20°C is described in [6]. On feeding the slurry continuously on to preheated CaSO_4 (120 to 200°C), HF is evolved [6], see also [7]. A mobile slurry can also be formed with an inert liquid like 1,2,4-trichlorobenzene [8].

Some patents deal with fluidized bed processes in which CaF_2 reacts with sulfuric acid vapor or with SO_3 and water vapor. This method is interesting in respect to the better exploitation of the raw material and the improved heat transfer. One procedure involves fluidizing the solid CaSO_4 by-product and heating the fluidized bed up to 300°C with CO_2 (1.5 atm and 600°C) from burning coke in air [9]. To this fluidized bed is added a 1:1 mixture of 98% CaF_2 and 100% H_2SO_4 [9, 10], which are heated by the CaSO_4 . The gas is

conducted through a condenser cooled to -70°C , which removes 99% of the HF produced [9]. A similar reactor produces HF of 98% purity [11] by mixing a preheated spray of powdered CaF_2 with a preheated spray of H_2SO_4 at 150 to 300°C . The CaSO_4 crystallizes into dry porous grains [11 to 13]. HF can be produced by the reaction of CaF_2 with gaseous H_2SO_4 , steam, and air, which is the carrier gas, at 330 to 370°C in a fluidized bed, the $\text{CaF}_2:\text{H}_2\text{SO}_4:\text{H}_2\text{O}$ molar ratio being 1:1.35:1.8. The yield of HF is 91% based on the CaF_2 . This reaction is carried out so that no liquid phase appears in the reaction space. The CaSO_4 residue does not agglomerate, and no HSO_3F is formed [14], see also [15]. The manufacture of HF by the reaction of CaF_2 with SO_3 and H_2O vapor is described in [16, 17].

Finely ground CaF_2 is treated with hot H_2SO_4 , oleum, and the spent acid (initially cold acidified HF solution and cold pure HF solution) from the multistage countercurrent washing of the crude HF gas [18]. This reaction is carried out in a rotating tubular reactor [18] or three-stage reactor [19]. HF can also be produced from preheated CaF_2 ($>550^{\circ}\text{C}$) and H_2SO_4 (80 to 110°C) in a countercurrent heat exchanger. The reaction rate can be increased by adding CaO , SO_3 , and oleum [20]. A method for producing 99% HF ($<0.05\%$ H_2SO_4) by treating CaF_2 ($\text{SiO}_2 \approx 1\%$, $\text{CO}_3^{2-} \approx 1\%$) with drops of acid (HF:70%, H_2O :29%, H_2SO_4 :1%) for 30 min to 1 h at 120°C has been described in [21]. HF is produced by treating fluor spar with 92.5% H_2SO_4 in the presence of an oxidizing agent, such as H_2O_2 (0.05 to 0.1 wt%), which is introduced into the H_2SO_4 solution mixed with hydrofluoric acid (≈ 0.04 wt%) [22]. Decomposing fluor spar with H_2SO_4 at 160 to 280°C , followed by thermal treatment of the reaction mass at 250 to 270°C in a current of air, produces HF [23].

SO_3 , H_2SO_4 , and fluor spar react to form HFSO_3 , which is then decomposed by H_2O into H_2SO_4 and HF of high purity. The gases leaving the fluor spar furnace are passed through a condenser operating at 25 to 45°C to remove substantially all of the HSO_3F . To keep the hydrolysis of HSO_3F under control the fluorosulfonic acid is passed through a number of hydrolysis chambers [24]. A limited amount of water is slowly added to each chamber [24]. Contamination with diluent gases including SiF_4 does not impair the conversion from HF into HSO_3F by reaction with SO_3 [25].

References:

- [1] G. Parisot, Société d'Électrochimie, d'Électrometallurgie et des Aciéries Électriques d'Ugine (U.S. 3300279 [1964/77]). – [2] G. Parisot, Société d'Électrochimie, d'Électrometallurgie et des Aciéries Électriques d'Ugine (Fr. 1356982-Add. 85022 [1963/65] from C.A. 64 [1966] 4654). – [3] A. Redniss (U.S. 3063815 [1959/62] from C.A. 58 [1963] 5287). – [4] W. E. Watson, R. P. Troeger, Allied Chemical Corp. (U.S. 3718736 [1969/73]; C.A. 79 [1973] No. 33246). – [5] C. C. Quarles, DuPont de Nemours (U.S. 3071437 [1959/63]; C.A. 58 [1963] 7634).
- [6] S. C. Carson, Imperial Chemical Ind. (U.S. 3404953 [1964/65]). – [7] W. Schabacher (in: Ullmanns Encyklopädie der technischen Chemie, 4th Ed., Vol. 11, Weinheim/Bergstr. 1976, pp. 598/606). – [8] J. C. Yacoe, DuPont de Nemours (U.S. 2846290 [1955/58]; C.A. 1958 19038). – [9] D. B. Burkhardt (U.S. 3207579 [1961/65]; C.A. 63 [1965] 17527). – [10] W. Faber, Riedel de Haen AG (Ger. 939867 [1954/56]; C.A. 1958 14108).
- [11] H. Aiso, S. Nomura, T. Takeuchi, Daikin Kogyo Co. (Fr. 1550122 [1966/68]; C.A. 71 [1969] No. 114737). – [12] H. Aimune, S. Nomura, T. Takeuchi, Daikin Kogyo Co. (Japan. 71-05571 [1966/71] from C.A. 75 [1971] No. 23326). – [13] H. Aiso, K. Kato, T. Takeuchi, Daikin Kogyo Co. (Japan. 71-33214 [1969/71] from C.A. 76 [1972] No. 47834). – [14] G. Winkhaus, E. Schultze-Rhonhof, Vereinigte Aluminium-Werke AG (Ger. Offen.

2410534 [1974/75]; C.A. **84** [1976] No. 61920). – [15] C. B. Hayworth, R. H. Hutzler, A. W. Michener, R. Sobel, Allied Chemical Corp. (Ger. 1 245 339 [1961/67] from C.A. **67** [1967] No. 74984).

[16] C. C. Quarles, DuPont de Nemours (U.S. 3 278 265 [1965/66]; C.A. **65** [1966] 19742). – [17] D. McMillan, C. C. Quarles, DuPont de Nemours (U.S. 3 102 787 [1960/63]; C.A. **60** [1964] 220). – [18] R. Gentili, Buss AG (Swiss 495 283 [1967/70]; C.A. **74** [1971] No. 33151). – [19] R. Gentili, Buss AG (Swiss 540 195 [1970/73]; C.A. **80** [1974] No. 49853). – [20] W. Schabacher, H. Rohe, H. Guth, W. Keller, Bayer AG (Ger. 2 103 338 [1971/72]; C.A. **77** [1972] No. 154571).

[21] D. Zanon, R. Trupiano, I.C.P.M.S.p.A. (U.S. 2 991 155 [1959/61]). – [22] A. L. Goldinov, E. I. Romanov, O. B. Abramov, A. P. Shishkanov (U.S.S.R. 462 799 [1972/75]; C.A. **83** [1975] No. 100223). – [23] B. P. Zverev, A. L. Goldinov, L. V. Sushinsteva, A. A. Shabalin (U.S.S.R. 167 833 [1963/65]; C.A. **63** [1965] 275). – [24] W. F. Mitchell, J. A. Grant-Mac Kay, Pennsylvania Salt. Man. Co. (U.S. 2 702 233 [1949/55]; C.A. **1955** 8571). – [25] W. F. Mitchell, J. A. Grant-MacKay, Pennsylvania Salt. Man. Co. (U.S. 2 753 245 [1954/56]; C.A. **1956** 15037).

2.1.1.2.2.2 Manufacture from CaF_2 without the Use of H_2SO_4

HF can be produced by the hydrothermal process $\text{CaF}_2 + \text{SiO}_2 + \text{H}_2\text{O} \xrightarrow{\text{heat}} \text{CaSiO}_3 + 2\text{HF}$ at ≈ 1925 to 2760°C , which gives an 80% conversion of H_2O to 90% HF. The heat is provided by an electrically augmented burner in which a hydrocarbon gas (CH_4 , C_3H_8 , fuel oil) is burned in air, O_2 , or oxygen-enriched air to form the steam [1].

A fluorite concentrate (CaF_2 95%; SiO_2 1 to 3%; H_2O 1%) can be treated 3 h with H_3PO_4 to give HF in a 90% yield based on the fluorine in the concentrate [2].

A molded mixture of powdered siliceous matter, CaF_2 or lower grade CaF_2 (< 50%) [4], and CaSiO_3 is calcined at 1000 to 1300°C [3 to 5] with steam to produce HF and $\alpha\text{-CaSiO}_3$ or pseudowollastonite $\text{Ca}_3[\text{Si}_3\text{O}_9]$. Even if the lower grade CaF_2 is used, the CaF_2 is > 97% defluorinated [3].

HF can be produced simultaneously with Portland cement clinker [6] or NaAlO_2 [7].

References:

[1] J. S. Hayford, Stauffer Chemical Corp. (U.S. 3 719 747 [1971/73]; C.A. **79** [1973] No. 33247). – [2] A. L. Klimov, B. G. Zotov, A. A. Gaidenko, V. J. Argunova (U.S.S.R. 178 796 [1965/66]; C.A. **65** [1966] 3393). – [3] H. Sato, M. Asanov, E. Eguchi, Onoda Chemical Ind. Co. (Japan. Kokai 73-37390 [1971/73] from C.A. **79** [1973] No. 94134). – [4] H. Sato, M. Asano, K. Eguchi, Onoda Cement Ind. Co. (Japan. Kokai 73-45488 [1971/73] from C.A. **79** [1973] No. 127853). – [5] H. Sato, M. Asano, E. Eguchi, Onoda Cement Co. (Japan. Kokai 73-45489 [1971/73] from C.A. **79** [1973] No. 127854).

[6] J. Kamlet (U.S. 3 017 246 [1960/62]; C.A. **56** [1962] 11244). – [7] K. G. Hrishikesan, F. E. Adkins, Reynolds Metals Co. (U.S. 3 116 971 [1961/64]).

2.1.1.2.3 Manufacture from H_2SiF_6

2.1.1.2.3.1 General Remarks

H_2SiF_6 is obtained as a by-product from the acidulation and concentration steps of wet-process H_3PO_4 production and from phosphate fertilizer production. Because of the enormous supply of fluorine in phosphate rock reserves and the large amount of fluorine