FLUORINE

1. Introduction

Fluorine [7782-42-4], F_2, is a diatomic molecule existing as a pale yellow gas at ordinary temperatures. Its name is derived from the Latin word fleure, meaning to flow, alluding to the well-known fluxing power of the mineral fluorite [7789-75-5], CaF_2, which is the most abundant naturally occurring compound of the element. Although radioactive isotopes between atomic weight 17 and 22 have been artificially prepared and have half-lives between 4 s for ^{22}F and 110 min for ^{18}F, fluorine has a single naturally occurring isotope, ^{19}F, and has an atomic weight of 18.9984 (1). Fluorine, the most electronegative element and the most reactive nonmetal, is located in the upper right corner of the Periodic Table. Its electron configuration is $1s^2 2s^2 2p^5$.

The only commercially feasible method of preparing elemental fluorine is by the electrolysis of molten fluoride-containing salts. Fluorine was first isolated in 1886 by the French chemist Moissan (2) who applied a method originally suggested and unsuccessfully tried by Davey and Ampere in 1810–1812. Moissan used potassium fluoride in anhydrous hydrogen fluoride resulting in an electrically conductive electrolyte. The only chemical route, which does not rely on compounds derived from F_2, has more recently been discovered (3). Both starting materials are easily prepared from HF, and react at 150°C evolving fluorine gas.

$$K_2MnF_6 + 2\ SbF_5 \longrightarrow 2\ KSbF_6 + MnF_3 + 1/2\ F_2$$

Fluorine was first produced commercially ~50 years after its discovery. In the intervening period, fluorine chemistry was restricted to the development of various types of electrolytic cells on a laboratory scale. In World War II, the demand for uranium hexafluoride [7783-81-5], UF_6, in the United States and the United Kingdom, and chlorine trifluoride [7790-91-2], ClF_3, in Germany, led to the development of commercial fluorine-generating cells. About 50% of the fluorine produced is used to make UF_6 for the nuclear power industry (see NUCLEAR REACTORS). Other large uses include the production of nitrogen trifluoride, sulfur hexafluoride, tungsten hexafluoride, carbon tetrafluoride, and hexafluoroethane. Fluorine, which does not occur freely in nature except for trace amounts in radioactive materials, is widely found in combination with other elements, accounting for ~0.065 wt% of the earth's crust (4). The most important natural source of fluorine for industrial purposes is the mineral fluorspar [14542-23-5], CaF_2, which contains ~49% fluorine. Detailed annual reports regarding the worldwide production and reserves of this mineral are available (5). A more complete discussion of the various sources of fluorine-containing minerals is given elsewhere (see FLUORINE COMPOUNDS, INORGANIC).

2. Physical Properties

Fluorine is a pale yellow gas that condenses to a yellowish orange liquid at −188°C, solidifies to a yellow solid at −220°C, and turns white in a phase

Table 1. **Physical Properties of Fluorine**

Property	Value	References
melting point, °C	-219.61^a	6
	-217.9	7
	-223	8
boiling point, °C	-188.13^a	6
	-187.7	7
	-187.0	8
	-188.22	9
	-188.03	10
solid transition temperature, °C	-227.60	6
critical temperature, °C	-129.2^a	11
	-129.00	9
critical pressure, kPa[b]	5571	(9,11)
heat of vaporization, ΔH_{vap}, at -188.44°C and 98.4 kPa, J/mol[c]	6544	6
heat of fusion, ΔH_{fus}, J/mol[c]	510	6
heat of transition, J/mol[c]	727.6	6
heat capacities, J/(mol · K)[c]		
solid at -223°C	49.338	6
at -238°C	31.074	6
	23.267	7
at -253°C	12.987	6
	9.372	7
liquid	57.312^a	6
	45.35	7
gas, C_p	31.46^a	12
	31.456	13
	31.380	14
	31.325	15
density of liquid at bp, kg/m^3	1516^a	16
	1514	17
density of solid, kg/m^3	1900^d	18
refractive index		
liquid at bp	1.2	19
gas at 0°C and 101.3 kPa[b]	1.000214	20
surface tension, liquid, mN/m(=dyn/cm)		
at -193.26°C	14.81	21
at -192.16°C	14.60	16
viscosity, mPa·s(= cP)		
liquid at -187.96°C	0.257	16
at -203.96°C	0.414	16
gas at 0°C and 101.3 kPa[b]	0.0218	22
	0.0209	7
thermal conductivity, gas at 0°C and 101.3 kPa, W/(m · K)	0.02477	23
dielectric constant, ε		
at -189.95°C	1.517	7
at -215.76°C	1.567	7
vapor pressure, kPa[b]		
at 53.56 K	0.22	6
at 63.49 K	2.79	6
at 72.56 K	18.62	6
at 83.06 K	80.52	6
at 89.40 K	162.11	6

[a] Generally accepted value.

[b] To convert kPa to mm Hg, multiply by 7.5.

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

[d] Mean estimate value.

transition at −228°C. Fluorine has a strong odor that is easily detectable at concentrations as low as 20 ppb. The odor resembles that of the other halogens and is comparable to strong ozone (qv).

Because of the extreme difficulty in handling fluorine, reported physical properties (Table 1) show greater than normal variations among investigators. A detailed summary and correlation of the physical, thermodynamic, transport, and electromagnetic properties of fluorine is given in Ref. 20.

3. Chemical Properties

Fluorine is the most reactive element, combining readily with most organic and inorganic materials at or below room temperature. Many organic and hydrogen-containing compounds, in particular, can burn or explode when exposed to pure fluorine. With all elements except helium, neon, and argon, fluorine forms compounds in which it shows a valence of −1. Fluorine reacts directly with the heavier helium-group gases xenon, radon, and krypton to form fluorides (see HELIUM GROUP GASES, HELIUM GROUP COMPOUNDS).

Fluorine is the most electronegative element and thus can oxidize many other elements to their highest oxidation state. The small size of the fluorine atom facilitates the arrangement of a large number of fluorines around an atom of another element. These properties of high oxidation potential and small size allow the formation of many simple and complex fluorides in which the other elements are at their highest oxidation states.

The reactivity of fluorine compounds varies from extremely stable, eg, sulfur hexafluoride [2551-62-4], and the perfluorocarbons (see FLUORINE COMPOUNDS, ORGANIC); to extremely reactive, eg, chlorine trifluoride and bromine trifluoride. Another unique property of nonionic metal fluorides is great volatility. Volatile compounds such as tungsten hexafluoride [7783-82-6], WF_6, and molybdenum hexafluoride [7783-77-9], MoF_6, are produced by the reaction of the particular metal with elemental fluorine.

Fluorine is the first member of the halogen family. However, many of its properties are not typical of the other halogens. Fluorine has only one valence state, −1, whereas the other halogens also form compounds in which their valences are +1, +3, +5, or +7. Fluorine also has the lowest enthalpy of dissociation relative to the other halogens, which is in part responsible for its greater reactivity. Furthermore, the strength of the bond fluorine forms with other atoms is greater than those formed by the other halogens.

Table 2 shows bond energies for the four diatomic molecular halogens, as well as for the halides of hydrogen, carbon, boron, and aluminum. Examination of these data indicates that the enthalpies of fluorination are much greater than those of other halogenations. Less energy is required to form fluorine molecules than that needed for chlorine or bromine molecules, and much more energy is evolved in the formation of the fluorides. Therefore, fluorination reactions occur more readily, generating intense heat, and these frequently occur in situations where other halogenations do not.

3.1. Reactions. *Metals.* At ordinary temperatures, fluorine reacts vigorously with most metals to form fluorides. A number of metals, including magnesium aluminum, copper, iron, and nickel, form an adherent and protective

Table 2. **Average Bond Energies, kJ**[a,b]

Halogen	XX[c]	HX[d]	BX_3[d]	AlX_3[e]	CX_4[d]
F	157.8	569	645	582	456
Cl	243.6	431	444	427	327
Br	193.0	368	368	360	272
I	151.1	297	272	285	239

[a] To convert J to cal, divide by 4.184.
[b] X = halogen.
[c] Ref. 24.
[d] Ref. 25.
[e] Ref. 26.

surface film of the metal fluoride salt thus allowing the metal's use in the storage and handling of the gas. A metal's susceptibility to reaction with fluorine depends, to a great extent, on its physical state. For example, powdered iron of 0.84-mm size (20 mesh) is not attacked by liquid fluorine, whereas in the 0.14-mm size (100 mesh) it ignites and burns violently. There is no apparent reaction between liquid fluorine and powdered nickel as fine as 0.14 mm. Massive copper burns at 692°C, whereas copper wool ignites at a much lower temperature. Nickel burns in fluorine at 1147°C, and aluminum burns above its melting point (27).

Tin reacts completely with fluorine >190°C to form tin tetrafluoride [7783-62-2], SnF_4. Titanium reacts appreciably >150°C at a rate dependent on the size of the particles; the conversion to titanium tetrafluoride [7783-63-3], TiF_4, is complete >200°C. Fluorine reacts with zirconium metal >190°C. However, the formation of a coating of zirconium tetrafluoride [7783-64-4], ZrF_4, prevents complete conversion, the reaction reaching only 90% completion even at 420°C (28). Tungsten powder reacts with fluorine at a temperature >250°C to produce the volatile tungsten hexafluoride, WF_6.

Nonmetals. Sulfur reacts with fluorine to yield the remarkably stable sulfur hexafluoride, SF_6. Operating conditions must be controlled because a mixture of the lower fluorides such as disulfur difluoride [13709-35-8], S_2F_2, disulfur decafluoride [5714-22-7], S_2F_{10}, and sulfur tetrafluoride [7783-60-0], SF_4, may also be formed. When this reaction is carried out between 310 and 340°C, SF_4 is primarily obtained and essentially no SF_6 and only trace amounts of lower fluorides. Below 300°C, and preferably at ~275°C, SF_6 is the primary product. At 450–500°C, a mixture comprising ~50% SF_4 and the lower sulfur fluorides is formed (see FLUORINE COMPOUNDS, INORGANIC SULFUR FLUORIDES).

Silicon and boron burn in fluorine forming silicon tetrafluoride [7783-61-1], SiF_4, and boron trifluoride [7637-07-2], BF_3, respectively. Selenium and tellurium form hexafluorides, whereas phosphorus forms tri- or pentafluorides. Fluorine reacts with the other halogens to form eight interhalogen compounds (see FLUORINE COMPOUNDS, INORGANIC, HALOGENS).

Water. Fluorine reacts with water to form hydrofluoric acid [7664-39-3], HF, and oxygen difluoride [7783-41-7], OF_2. In dilute (< 5%) caustic solutions, the reaction proceeds as follows:

$$2\,F_2 + 2\,NaOH \longrightarrow OF_2 + 2\,NaF + H_2O$$

In the presence of excess caustic, the oxygen difluoride is gradually reduced to oxygen and fluoride:

$$OF_2 + 2\,NaOH \longrightarrow 2\,NaF + O_2 + H_2O$$

The overall reaction under controlled conditions provides a method for the disposal of fluorine by conversion to a salt:

$$2\,F_2 + 4\,NaOH \longrightarrow 4\,NaF + O_2 + 2\,H_2O$$

Oxygen. Oxygen does not react directly with fluorine under ordinary conditions, although in addition to oxygen difluoride, three other oxygen fluorides are known (29). Dioxygen difluoride [7783-44-0], O_2F_2, trioxygen difluoride [16829-28-0], O_3F_2, and tetraoxygen difluoride [12020-93-8], O_4F_2, are produced in an electric discharge at cryogenic temperatures by controlling the ratio of fluorine to oxygen.

Nitrogen. Nitrogen usually does not react with fluorine under ordinary conditions and is often used as a diluent to moderate fluorinations. However, nitrogen can be made to produce nitrogen trifluoride, NF_3, by radiochemistry (30), glow discharge (31), or plasma (32) synthesis (see PLASMA TECHNOLOGY).

Noble Gases. Fluorine has the unique ability to react with the heavier noble gases to form binary fluorides. Xenon reacts at room temperature under uv radiation forming xenon difluoride [13709-36-9], XeF_2 (16–18,21,33,34). Xenon tetrafluoride [13709-61-0], XeF_4, is obtained by mixing an excess of fluorine with xenon and heating the mixture to 400°C (33,35). Fluorine and xenon at 300°C under 6–6.8 MPa (60–67 atm) yield the xenon hexafluoride [13693-09-9], XeF_6 (36,37). Fluorine reacts with radon at 400°C to yield a compound of low volatility, probably the difluoride (38). Krypton reacts with fluorine in an electric discharge at liquid air temperatures to yield krypton difluoride [13773-81-4], KrF_2 (39).

Hydrogen. The reaction between fluorine and hydrogen is self-igniting and extremely energetic. It occurs spontaneously at ambient temperatures as evidenced by minor explosions that sometimes occur in fluorine-generating cells from the mixing of the H_2 and F_2 streams. The controlled high temperature reaction of fluorine atoms, whether generated thermally or photolytically from fluorine gas, with hydrogen or deuterium is an energy source for high power chemical lasers (qv) (40). However, NF_3 has become the preferred fluorine source because it is easier to handle (41).

Ammonia. Ammonia (qv) reacts with excess fluorine in the vapor phase to produce N_2, NF_3, N_2F_2, HF, and NH_4F. This reaction is difficult to control in the vapor phase because of the intense heat of reaction, and in some cases only N_2 and HF are produced. Nitrogen trifluoride was obtained in 6% yields in a gas-phase reaction over copper (42). Yields of more than 80% are achieved by the reaction of fluorine and ammonia in a molten ammonium acid fluoride solution (43,44).

Organic Compounds. The reaction of pure or undiluted fluorine and organic compounds is usually accompanied by either ignition or a violent explosion of the mixture because of the very high heat of reaction. However, useful commercial-scale syntheses using fluorine are undertaken. Volatile compounds may be fluorinated in the gas phase by moderating the reaction using an inert gas such as nitrogen, by reducing reaction temperatures ($\leq -78°C$), and/or by the presence of finely divided packing materials. Solutions or dispersions of higher boiling materials may be fluorinated in inert solvents such as 1,1,2-trichloro-1,2,2-trifluoroethane [76-13-1] or some perfluorocarbon fluids, eg, Fluorinert FC-27 or FC-75 (3M) (45,46). Efficient removal of the very high reaction heat, which leads to molecular fragmentation and runaway reactions, is the underlying principle in any of the aforementioned approaches.

Saturated hydrocarbons (qv) under controlled conditions react with elemental fluorine to produce perfluorocarbons; the reaction is usually accompanied by some fragmentation and polymerization (47,48). The fluorination of aromatic compounds gives degradation products, polymers, unstable unsaturated compounds, or highly fluorinated cyclohexane derivatives, but no aromatic compounds. Methanol (qv) and acetone (qv) produce a variety of fluorinated carbonyl compounds (49–51). Various polyethers have been successfully fluorinated to give perfluoropolyethers in high yields (45,46) (see FLUORINE COMPOUNDS, ORGANIC, DIRECT FLUORINATION). Fluorine is also used in the preparation of cobalt trifluoride [10026-18-3], CoF_3, and other higher oxidation state metal fluorides, which can be used in high temperature fluorinations of aliphatic compounds (52).

Selective fluorination, where only one or two fluorines are introduced into a molecule, is becoming more prominent. One well-known example is the direct fluorination of uracil (2,4-pyrimidinedione), $C_4N_2H_4O_2$, in aqueous solution to produce 5-fluorouracil [51-21-8] (5-fluoro-2,4-pyrimidinedione), $C_4N_2H_3FO_2$ (53). Greater selectivity in the fluorination of substituted aromatics has been achieved in acids having a dielectric constant >20 and pH <3 (54). Sulfuric and formic acids were found to be particularly advantageous. Certain nitrogen- and oxygen-containing organics react with fluorine to yield a group of compounds known as electrophilic fluorinating agents (55–58). These reagents are used in regiospecific fluorinations of other organic substrates, particularly those used in pharmaceuticals (qv). For more information regarding selective fluorination, see Refs. 59–61.

Polymers. The dilution of fluorine using an inert gas significantly reduces the reactivity, thus allowing controlled reactions to take place with hydrocarbon polymers, even at elevated temperatures. High density polyethylene containers can be blow-molded using 1–10% fluorine in nitrogen mixtures to produce barrier layers on the inside of the containers (see BARRIER POLYMERS; OLEFIN POLYMERS) (62). The permeation rate of nonpolar solvents such as *n*-pentane can be reduced by a factor of almost 500 when containers are blow-molded with a 1% fluorine-in-nitrogen mixture (63,64). Mixtures of 1–10% fluorine in nitrogen have been used to improve the surface properties, ie, moisture transport, soil release, and soil redeposition, of polyester, polyamide, polyolefin, and polyacrylonitrile fibers (65,66) (see FIBERS, POLYESTER; POLYAMIDES, FIBERS).

Fluorine may also be used in conjunction with other reactive gases, eg, oxygen and water vapor, to activate polymer surfaces in order to improve chemical bonding and adhesion (67). For example, ethylene–propylene–diene monomer (EPDM) rubber moldings exposed to a very dilute fluorine mixture, eg, 1–5% F_2 in N_2, and subsequently to atmospheric oxygen and moisture have higher surface energy and can be bonded with adhesives (qv) (68). Adhesives do not wet and thus do not adhere to the untreated rubber. Fluorine activates the polymer surface by initiating reactions which form reactive C–OH, C–OOH, or C–OF surface groups. Also, contaminates such as plasticizers (qv) and polymer processing aids are oxidized and removed from the surface. Similarly, other materials including polyolefins (69), polyethylene–vinyl acetate foams (70), and rubber tire scrap (71), can be treated with fluorine.

Carbon and Graphite. Fluorine reacts with amorphous forms of carbon, such as wood charcoal, to form carbon tetrafluoride [75-73-0], CF_4, and small amounts of other perfluorocarbons. The reaction initiates at ambient conditions, but proceeds to elevated temperatures as the charcoal burns in fluorine.

Fluorine reacts with high purity carbon or graphite at elevated temperatures under controlled conditions to produce fluorinated carbon, $(CF_x)_n$. Compounds having colors ranging from black to white have been prepared with fluorine contents ranging from $x = 0.1$ to $x = 1.3$ (72–76). The material was first obtained (72) in 1934, when graphite was heated to 420–460°C in a stream of fluorine to produce a gray product of composition $CF_{0.92}$. Subsequently, a white material of composition $CF_{1.12}$ was obtained (73) by accurate control of the reaction temperature to 627 ± 3°C. Applications utilizing the unique properties of these materials began to be developed in the late 1960s. Fluorinated carbon is a specialty product used in lithium batteries (qv) (78) and lubricants (77). For a complete review of these materials see Refs. 79 and 80.

4. Manufacture

Fluorine is produced by the electrolysis of anhydrous potassium bifluoride [7789-29-9], KHF_2 or $KF{\cdot}HF$, which contains various concentrations of free HF. The fluoride ion is oxidized at the anode to liberate fluorine gas, and the hydrogen ion is reduced at the cathode to liberate hydrogen. Anhydrous HF cannot be used alone because of its low electrical conductivity (see ELECTROCHEMICAL PROCESSING, INORGANIC).

Fluorine-generating cells are classified into three distinct types, based on operating temperatures: low (−80–20°C) temperature cells, medium (60–110°C) temperature cells, and high (220–300°C) temperature cells. Figure 1 is a melting point diagram for the KF–HF system showing the three distinct areas of temperature operation and the corresponding HF concentrations in the electrolyte. Reference 81 presents a complete description of various laboratory and industrial fluorine cells worldwide.

Cells operating at low (2,82,83) and high (81,84) temperatures were developed first, but discontinued because of corrosion and other problems. The first medium temperature cell had an electrolyte composition corresponding to $KF \cdot 3HF$, and operated at 65–75°C using a copper cathode and nickel anodes. A later cell operated at 75°C and used $KF{\cdot}2.2HF$ or $KF{\cdot}2HF$ as electrolyte (85,86), and nickel and graphite as anode materials.

4.1. Commercial Cells. All commercial fluorine installations employ medium temperature cells having operating currents of ≥5000 A. The medium temperature cell offers the following advantages over low and high temperature

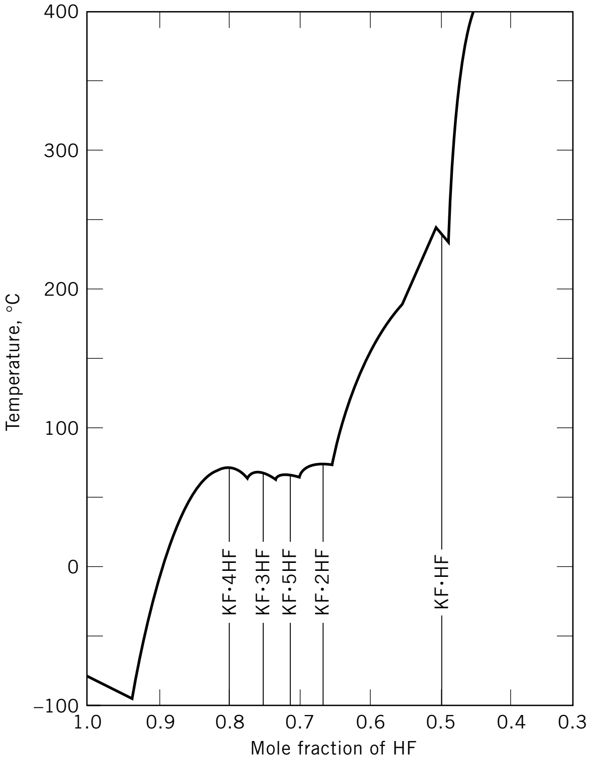

Fig. 1. Phase diagram of the potassium fluoride–hydrogen fluoride system.

cells: (*1*) the vapor pressure of HF over the electrolyte is less; (*2*) the composition of the electrolyte can vary over a relatively wide range for only a small variation in the operation of the cell; (*3*) less corrosion or deterioration of the anode occurs; (*4*) tempered water can be used as cell coolant; and (*5*) the formation of a highly resistant film on the anode surface is considerably reduced compared to the high temperature cell.

The C and E type of the Atomic Energy Commission (AEC) (now the Department of Energy) cell designs (87–90) predominate in the United States and Canada. These were developed by Union Carbide Nuclear Co., under the auspices of the AEC, as part of the overall manufacturing process for uranium hexafluoride, UF_6. Large fluorine-generating plants using these designs were installed at the Paducah, Oak Ridge, and Portsmouth gaseous diffusion plants (which are no longer in operation) (see DIFFUSION SEPARATION METHODS). The AEC designs have been made available to industry and are used by several commercial producers. The other cell type used in the United States is a proprietary design developed by Allied Chemical, Corp. (now Honeywell International, Inc.). This latter cell has a capacity of 5000 A and is used by Honeywell at its Metropolis, Illinois, plant. Table 3 gives the operating characteristics of a typical commercial size cell (AEC E-type).

Table 3. **AEC E-Type Cell Operating Characteristics**

Characteristic	Value
current, A	6000
operating voltage, V	9–12
cell operating temperature, °C	90–105
hydrogen fluoride in electrolyte, %	40–42
effective anode area, m^2	3.9
anode current density, A/m^2	1500
anodes	32
anode life, $A \cdot h$	$40 - 80 \times 10^6$

AEC Cell. A diagram of the AEC cell is shown in Figure 2. The main components are the cell tank, cell head, anode assembly, cathode assembly, screen diaphragm, and packing gland (86,90,91). The E- and C-type are similar in design and are both rated at 6000 A maximum capacity. The E-type incorporated

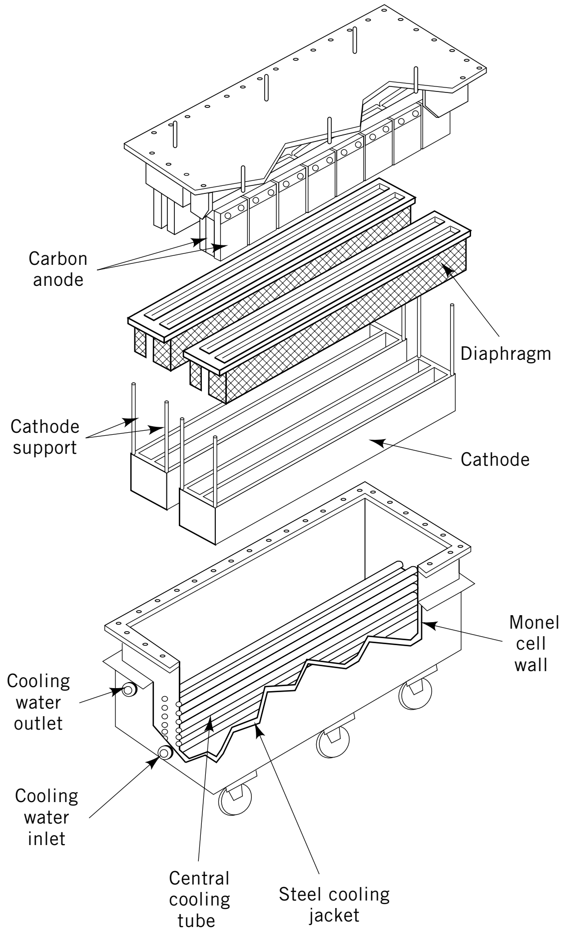

Fig. 2. Exploded view of AEC-type fluorine cell.

design changes to improve heat removal efficiency and to prolong life of the anode-contact connection. The cell tank is constructed of 95-mm Monel plate surrounded by a thin-gauge Monel jacket to overcome the corrosion problems encountered by using a steel jacket. A recessed bolt carbon-plug fastens the anodes to a copper support bar. This design gives improved cell life over the C-type copper pressure-plate design by using a steel anode support bar.

The cell head is fabricated from a 2.54-cm steel plate and has separate compartments for fluorine and hydrogen. The outlet-gas manifolds, hydrogen fluoride feed and purge lines, and electrical connections are on top of the head. The gas separation skirt is made of Monel. An insulating gasket maintains the seal between the tank and the head. The anode assembly consists of 32 carbon blades bolted onto a copper bar, each of which contains three copper conductor posts. The cathode assembly consists of three vertical, 0.6-cm parallel steep plates. The plates surround the anode assembly and are supported by three steel posts which also serve as conductors.

Allied Signal Cell. A cross-section of Honeywell's cell is shown in Figure 3. The cell body is a rectangular steel box on wheels with an outside water-cooling jacket. A central partition divides the box lengthwise. The negative side of the dc bus is connected directly to the cell container. The interior of the box and the central partition act as the cathodic area of the cell.

Other Cell Designs. Although not used in the United States, another important cell is based on designs developed by ICI (92). Cells of this type are used by British Nuclear Fuels plc and differ from the cells shown in Figures 2 and 3 in two ways: (*1*) the anodes used are made of the same hard, nongraphitized carbon, but are more porous; and (*2*) the cathodes are formed from coiled tubes and provide additional cooling (93).

Anodes. Fluorine cell anodes are the most important cell component, and their design and materials of construction are key factors in determining productivity and cell life. Nickel and graphite, used in early cells, were abandoned when it was discovered that hard, nongraphitized carbon gave longer life. Today, anodes are made from petroleum coke and a pitch binder that is calcined at temperatures below that needed to convert the material to graphite. The anode carbon has low electrical resistance, high physical strength, and is resistant to reaction with fluorine. Historically, Union Carbide's YBD-grade carbon made the best anodes. More recently other carbon manufacturers have begun to offer improved anodes for fluorine service, eg, Carbone of America Ind. Corp.; Sociétè Des Electrodes et Refractaires Savoié, part of the Pechiney group; and Toyo Tanso USA, Inc. The nature and quality of the starting materials (petroleum coke and pitch) and careful control of the calcining process are generally responsible for the improvements (94).

About 30% of the cell's operating voltage (9–12 V) is consumed by the anode overvoltage. Although some electrode overvoltage is common in all electrochemical processes, 3–4 V is exceptional. There are three generally accepted reasons for the high anode overvoltage: ohmic overvoltage, bubble overvoltage, and inhibition of charge transfer. Ohmic losses are generally small and result from the resistivity of the anode carbon and contact resistance between the anode and the metal current carriers. However, severe losses can arise if the contact between the anode and the current carrier becomes corroded. All commercial

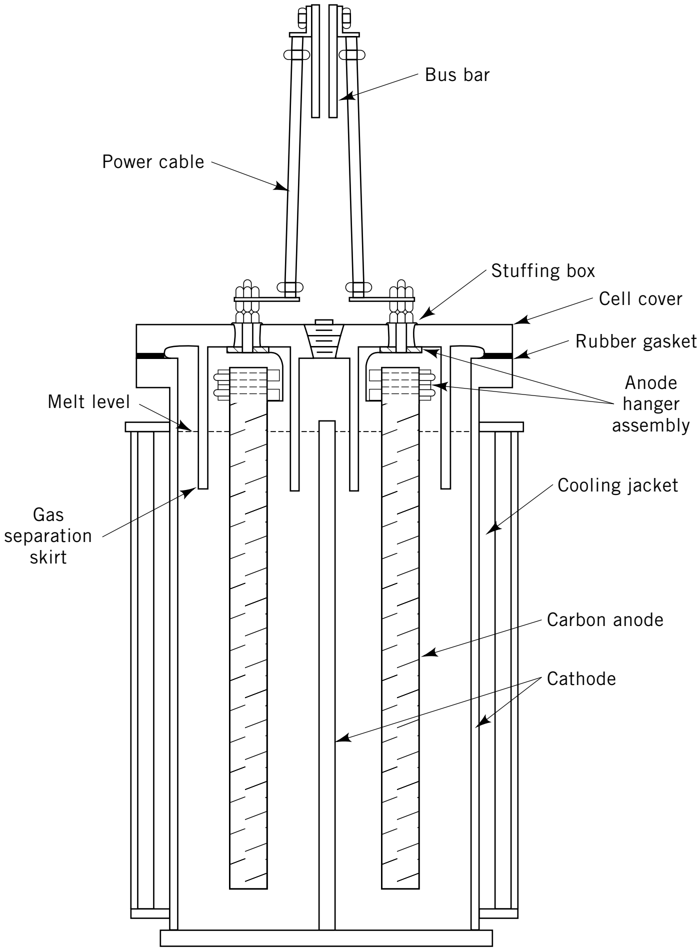

Fig. 3. Fluorine generator. (Courtesy of Allied Signal, Inc.)

fluorine producers have proprietary designs for these connections, which mitigate this problem.

Bubble overvoltage and inhibition of charge transfer are related problems that are caused by the formation of a layer of fluorinated carbon, $(CF_x)_n$, on the anode surface (95,96). Because this material has very low electrical conductivity and is strongly nonwetting, electronic charge transfer is impeded and contact with the electrolyte is lost. As a result of the nonwetting character of the $(CF_x)_n$, bubbles of fluorine gas cling to the anode and grow in size, thereby reducing its effective surface area. Localized hot spots within the cell usually form under these conditions as the remaining working portions of the anode are subjected to higher than normal current densities. The locally excessive temperature also leads to the deterioration or burning of the anode. Signs of this problem are higher than normal cell voltage and higher levels of CF_4 in the fluorine product stream. In extreme cases the working surfaces of the anodes may become so restricted that fluorine production ceases.

Studies of anode electrochemistry have shown that water (>500 ppm) in the electrolyte can increase the formation of $(CF_x)_n$ on the anode surface (97). Under normal operating voltages, carbon can be electrochemically oxidized in the presence of water to form a graphite oxide, C_xO, film on the electrode surface, which then readily reacts with fluorine to form $(CF_x)_n$. Highly graphitic forms of carbon are much more susceptible to this problem. By starting out new cells at lower than normal operating voltages (6 V or less) trace amounts of water may be electrolyzed to H_2 and O_2 and removed from the cell, while avoiding the formation of C_xO.

Further improvements in anode performance have been achieved through the inclusion of certain metal salts in the electrolyte, and more recently by direct incorporation into the anode (95,98,99). Good anode performance has been shown to depend on the formation of carbon–fluorine intercalation compounds at the electrode surface (100). These intercalation compounds resist further oxidation by fluorine to form $(CF_x)_n$, have good electrical conductivity, and are wet by the electrolyte. The presence of certain metals enhance the formation of the intercalation compounds. Lithium, aluminum, or nickel fluoride appear to be the best salts for this purpose (94,100).

Other Cell Components. American fluorine manufacturers use Monel or steel cathodes. The early German investigators used magnesium cathodes without excessive corrosion in the high temperature cells. Welded steel or Monel construction is used for the cell body. Skirts are used to separate the hydrogen and fluorine above the electrolyte. The solid metal skirt is welded to the cell cover plate and extends vertically downward 10–15 cm into the electrolyte. In the AEC cells, the skirt extends further into the electrolyte as a wire mesh. This extension is called the diaphragm and acts to direct the flow of gases as they are liberated. The AEC cells use Monel skirts and diaphragms. The Honeywell cell uses a magnesium alloy skirt and does not employ a diaphragm.

Polytetrafluoroethylene (PTFE) provides the most satisfactory electrical insulation. Concentric rings of PTFE and PTFE impregnated with calcium fluoride are used for the packing glands which support the anode and cathode posts. Rubber is used as the gasket material to form a seal between the cover and the cell body.

Cells must be fitted with mild steel jackets and/or coils to remove heat during cell operation and to provide heat to maintain the electrolyte molten during shutdown. All commercial cells are totally jacketed. However, the accumulation of corrosive products can cause flow restrictions, resulting in decreased heat-transfer capacity. This problem was overcome in the AEC E-type cell by using a water jacket constructed of thin-gauge Monel with vertical corrugations to provide strength. The AEC cells also use internal Monel tubes, manifolded to the external jacket, for additional heat-transfer area. Because one of the operating limits is heat removal, improvements in jacket and tube design were a key factor in increasing the current-handling capacity of commercial cells.

4.2. Heat Transfer. A large portion of cell operating voltage is consumed in ohmic processes that generate heat and are a result of the large separation between anode and cathode and the resistivity of the electrolyte. Approximately 34.8 MJ (33,000 Btu) must be removed per kilogram of fluorine produced from any fluorine cell. This is accomplished by jacketing the cell and/or by using cooling tubes. The temperature of the cooling water should not drop <58°C in order to avoid crystallization of bifluoride on the cell wall (88).

4.3. Raw Materials. The principal raw material for fluorine production is high purity anhydrous hydrofluoric acid. Each kilogram of fluorine generated requires ~1.1 kg HF. Only a small portion of the hydrofluoric acid produced in the United States is consumed in fluorine production. The commercial grade is acceptable for use as received, provided water content is <0.02%. Typical specifications for hydrofluoric acid are

Assay	Wt %
HF, min	99.95
SO_2, max	0.005
H_2SiF_6, max	0.001
H_2O, max	0.02
nonvolatile acid (as H_2SO_4), max	0.01

Potassium bifluoride, $KF \cdot HF$, is used as a raw material to charge the cells initially and for makeup when cells are rebuilt. A newly charged cell requires ~1400 kg $KF \cdot HF$. Overall consumption of $KF \cdot HF$ per kilogram of fluorine generated is small. Commercial-grade flake potassium bifluoride is acceptable. Its specifications are

Assay	Wt %
$KF \cdot HF$, min	99.3
Cl, max	0.01
K_2SiF_6	0.50
SO_4, max	0.01
Fe, max	0.02
Pb, max	0.005
H_2O, max	0.10

4.4. Processes. The generation of fluorine on an industrial scale is a complex operation (91,101). The basic raw material, anhydrous hydrogen fluoride, is stored in bulk and charged to a holding tank from which it is continuously fed to the cells. Electrolyte for the cells is prepared by mixing $KF \cdot HF$ with HF to form $KF \cdot 2HF$. The newly charged cells are started up at a low current, which is gradually increased at a conditioning station separate from the cell operating position until full current is obtained at normal voltages. After conditioning, cells are connected in series using ca 12 V provided for each cell by a low voltage, 6000 A dc rectifier. Hydrogen fluoride content is maintained between 40 and 42% by continuous additions. The electrolyte level must be set and controlled at a certain level below the cell head in order to maintain a seal between the fluorine and hydrogen compartments. The cells are operated at 95–105°C and cooled with water at 75°C.

Approximately 142.3 MJ/h (135,000 Btu/h) must be removed at an operating current of 6000 A. The hydrogen and fluorine gas leaving the cell contains ~10 vol% HF. The individual gas streams from each cell are joined into separate hydrogen and fluorine headers for further processing in the plant. Demisters and filters are provided in the product gas streams to remove entrained electrolyte. The gas streams are then cooled to −78°C in refrigerant-cooled condensers to reduce the HF concentration to ~2 mol %. The condensed HF is recycled, and hydrogen stream is scrubbed with a caustic solution and vented or burned. Several possibilities are available for utilizing the fluorine stream. If <3% HF levels are required, sodium fluoride towers or further cooling are employed to freeze out the HF and reduce the concentration to <0.2 mol %. Compressors or exhausters are normally required in both fluorine and hydrogen streams at some point in the system beyond the HF condensers.

Figure 4 presents the equipment flow sheet for a 9-t/day fluorine plant.

4.5. Equipment. Fluorine can be handled using a variety of materials (102–105). Table 4 shows the corrosion rates of some of these as a function of temperature. System cleanliness and passivation are critical to success. Materials such as nickel, Monel, aluminum, magnesium, copper, brass, stainless steel, and carbon steel are commonly used. More information is available in the literature (20,106).

Copper, brass, and steel are generally used for gaseous service at temperatures <200°C; Monel and nickel are used at elevated temperatures. For critical applications and where there is any danger of temperature buildup, only nickel or Monel should be used because of the stability of the nickel fluoride film. Only highly fluorinated polymers, such as polytetrafluoroethylene, are resistant to the gas under nominally static conditions. The PTFE must be free of any impurities, dirt, or foreign materials that could initiate ignition with fluorine. However, fluoropolymers are more susceptible to ignition than metals, and thus should be used as little as possible in fluorine service, especially in contact with flowing streams at high velocities or pressures.

All equipment, lines, and fittings intended for fluorine service must be leak-tight, dry, and thoroughly cleansed of all foreign matter before use. The system should be checked for leaks, at least to its working pressure. It should be flushed with a nonaqueous degreasing solvent, such as methylene chloride, thoroughly purged with a stream of dry nitrogen, and evacuated to make certain no volatiles are present. Any foreign matter, particularly organics, not removed could burn with fluorine and initiate the burning of the metal equipment. After cleaning, the system should be filled with dry nitrogen.

The corrosion resistance of all materials used with fluorine depends on the passivation of the system. This is a pickling operation intended to remove the last traces of foreign matter, and to form a passive fluoride film on the metal surface. The dry nitrogen in the system is slowly replaced with gaseous fluorine in small increments until the concentration and pressure approach working conditions. Carbon steel is most commonly used for pipe and fittings (2.5 cm or greater) in gaseous fluorine service at ambient temperature conditions and pressures up to 2.86 MPa (415 psi).

Carbon steel or bronze-body gate valves are commonly used in gaseous fluorine service at low pressure. Plug valves, having Monel bodies and plugs, are

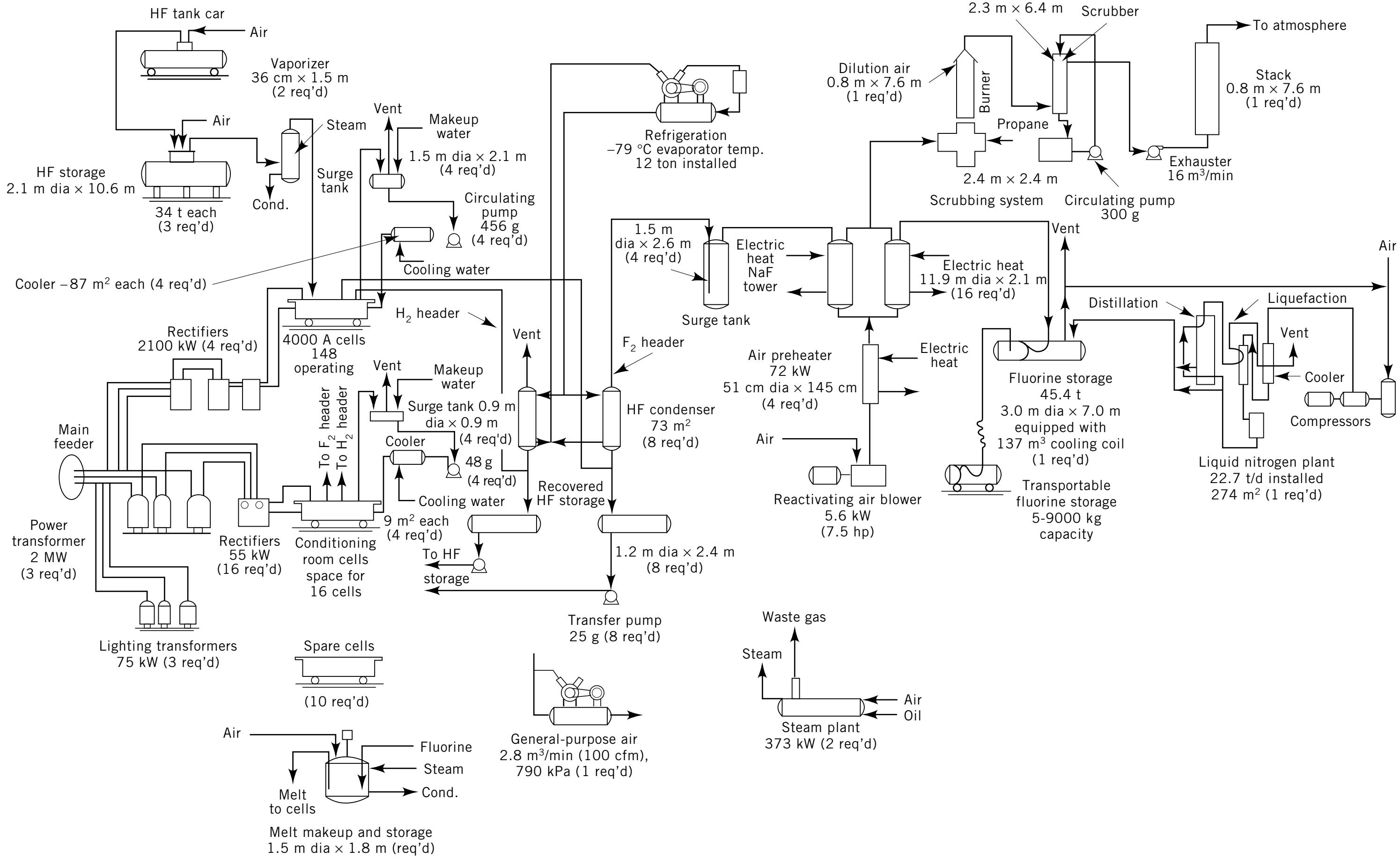

Fig. 4. Equipment flow sheet of elemental fluorine production and liquefaction plant, 9 t/day capacity. Step 1: purging residual F_2 at rates indicated; all but a trace of residual F_2 is removed in 15 min; N_2 purge is maintained for 1 h to remove last traces. Step 2: HF removal at rates indicated; all but a trace of HF is removed in 10 h; air purge is maintained for 10 h. To convert kPa to psi, multiply by 0.145.

Table 4. **Corrosion of Metals at Various Temperatures, mm/mo**[a]

	Tempeature, °C					
Material	200	300	400	500	600	700
nickel			0.018	0.129	0.74	0.86
Monel			0.013	0.051	1.5	3.8
Inconel			0.96	1.6	4.3	13
copper			4.1	3.0	25	74
aluminum			0	0.33	0.46	
magnesium	0	0				
iron	0	0.23	0.61	295		
steel						
0.27% carbon	0.051	0.23	0.38	503		
stainless, 310	0	0.79	14.2			

[a] Table abstracted from Ref. 104.

recommended for moderate pressure service <500 kPa (< 5 atm). For valve-stem packing PTFE polymer is recommended and it must be maintained leak-tight. Valves lubricated or packed with grease or other organics should never be used. Bellows-type valves having Monel or stainless steel bellows are recommended for high pressure service, but not ball valves.

Compressors and blowers for gaseous fluorine service vary in design from multistage centrifugal compressors to diaphragm and piston types. Standard commercial instrumentation and control devices are used in fluorine systems. Pressure is measured using Bourdon-type gauges or pressure transducers. Stainless steel or Monel construction is recommended for parts in contact with fluorine. Standard thermocouples are used for all fluorine temperature-measuring equipment, such as the stainless-steel shielded type, inserted through a threaded compression fitting welded into the line. For high temperature service, nickel-shielded thermocouples should be used.

Dilute mixtures (eg, 10 or 20% F_2 in N_2) are generally less hazardous than pure fluorine, but the same precautions and procedures should be employed.

5. Economic Aspects

Fluorine gas is packaged and shipped in steel cylinders conforming to Department of Transportation (DOT) specifications 3A1000 and 3AA1000 under a pressure of 2.86 MPa (415 psi). Table 5 lists world fluorine producers. Cylinders containing 2.2 and 0.7 kg are available from Airgas, Inc. All cylinders are equipped with special fluorine valves, the outlets of which have a left-hand thread conforming to the Compressed Gas Association (CGA) Specification 679 or 670. DOT regulations stipulate that cylinders must be shipped without safety relief devices and be equipped with valve protection caps. The total quantity of pure, gaseous fluorine in any size container is limited to 2.7 kg and the pressure must not exceed 2.86 MPa (415 psi) at 21°C.

Table 5. **Fluorine Producers**

Name	Location	Products[a]	Capacity[b]
Air Products and Chemicals	Allentown, Pa.	NF_3, SF_6, WF_6, ClF_3, BrF_3, CF_4, C_2F_6, fluorinating agents, F_2 gas	very large
Asahi Glass Co. Ltd	Tokyo, Japan	SF_6, IF_5	large
British Nuclear Fuels plc/Westinghouse	Preston, U.K.	UF_6, F_2 gas	large
Cameco, Port Hope Conversion Facility	Port Hope, Onatrio, Canada	UF_6	large
Central Glass Co. Ltd	Tokyo, Japan	NF_3,WF_6, ClF_3, $(CF_x)_n$, perfluorinated hydrocarbons	moderate
Comurhex (Pechiney group)	Paris, France	UF_6, WF_6, ClF_3, F_2 gas	large
Daikin Industries, Ltd.	Osaka, Japan	$(CF_x)_n$, IF_5, perfluorinated hydrocarbons, perfluoroether fluids	large
Exfluor Research	Round Rock, Texas	Perfluorinated alkanes, acids, and alcohols.	Small
Fluoro-Seal, Ltd.	Houston, Texas	Surface modified films, fibers, powders, and containers	moderate
Honeywell Inc.	Morristown, N. J.	UF_6, SF_6, IF_5, SbF_5	very large
Kanto Denka Kogyo Co., Ltd	Tokyo, Japan	NF_3, SF_6, WF_6, ClF_3, CF_4, C_2F_6, C_3F_8, C_4F_8, CHF_3	large
Pelchem, chemical division of NECSA	South Africa	NF_3, SF_6, WF_6, ClF_3, CF_4, XeF_2, perfluorinated hyrdrocarbon, F_2 gas	large
Showa Denko/ Air Products Co., Ltd.	Tokyo, Japan	CF_4, C_2F_6	large
Solvay Fluor	Hannover, Germany	SF_6, IF_5, perfluorinated hydrocarbons, perfluoroether fluids, fluoromonomers, F_2 gas	large

[a] The F_2 gas in the product list indicates that this company packages and sells fluorine.

[b] Categories of production capacity.

very large	4000 to 8000 ton/year
large	1000 to 3999 ton/year
moderate	500 to 999 ton/year
small	100 to 499 ton/year

Mixtures of 10 and 20% fluorine in nitrogen or other inert gases are commercially available in cylinders and tube trailers from Airgas, Inc. Blends can be safely packaged and stored at high, eg, 13.8 MPa (2000 psi), pressure. Filled with a 20% fluorine blend, tube trailers can contain up to 500 kg of fluorine. Such high pressure mixtures permit larger quantities of fluorine to be safely shipped.

5.1. Price. The 2002 U.S. price for fluorine in cylinders is $81.42/kg for 2.2 kg of gas. The price in large volumes is determined by (*1*) the price of hydrofluoric acid; (*2*) power costs, ca 4.5 kW·h electricity is required for each kilogram of fluorine produced; (*3*) labor costs; (*4*) costs to maintain and rebuild cells; and (*5*) amortization of fixed capital. Fluorine production is highly capital intense. In addition, purification, compression, packaging, and distribution in cylinders increase the cost significantly.

5.2. Manufacturer. Besides manufacturers in the United States, commercial fluorine plants are operating in Canada, France, Germany, Italy, Japan, the United Kingdom, and South Africa. (see Table 5). Fluorine is also produced in the Russia and China; however, details regarding its manufacture, production volumes, etc, are regarded as secret information. The total commercial production capacity of fluorine (excluding Russia and China) is estimated at ~20,000 t/year.

6. Analytical Methods

Direct analysis of gaseous fluorine is not possible by conventional methods because of its reactivity, therefore fluorine is converted (107) quantitatively to chlorine and the effluent stream analyzed. First, the fluorine sample is passed through a bed of sodium fluoride which retains the hydrogen fluoride. This step can be eliminated if the fluorine is free of HF as received. The sample is then passed over granular sodium chloride which reacts quantitatively with fluorine to release chlorine. This latter is reduced to chloride, which is determined by the Volhard method. Impurities such as oxygen, nitrogen, carbon tetrafluoride, sulfur hexafluoride, and carbon dioxide are determined by conventional gas chromatography techniques. Hydrogen fluoride is determined by infrared analysis of a separate sample. For processes using fluorine, the concentration may be monitored using uv analyzers such as those manufactured by Du Pont Instruments.

Fluorine in the atmosphere can be detected by chemical methods involving the displacement of halogens from halides. Dilute fluorine leaks are easily detected by passing a damp piece of starch iodide paper around the suspected area. The paper should be held with metal tongs or forceps to avoid contact with the gas stream and immediately darkens when fluorine is present.

Continuous monitoring for the presence of fluorine gas in the workplace may be accomplished using detectors available from Mine Safety Appliances (Pittsburgh, Pa.) or EIT (Exton, Pa.).

6.1. Specifications. Fluorine, having a dewpoint of −40°C and containing a maximum of 1.0 ppm water, is sold in cylinders according to the following specifications:

Assay	Mol %
fluorine, min	98
oxygen, max	0.5
nitrogen, max	1.0
carbon tetrafluoride, max	0.1
sulfur hexafluoride, max	0.1
hydrogen fluoride, max	0.2
carbon dioxide, max	0.1

7. Health and Safety Factors

Fluorine, the most reactive element known, is a dangerous material but may be handled safely using proper precautions. In any situation where an operator may come into contact with low pressure fluorine, safety glasses, a neoprene coat, boots, and clean neoprene gloves should be worn to afford overall body protection. This protection is effective against both fluorine and the hydrofluoric acid which may form from reaction of moisture in the air.

In addition, face shields made of conventional materials or, preferably, transparent, highly fluorinated polymers, should be worn whenever operators approach equipment containing fluorine under pressure. A mask having a self-contained air supply or an air helmet with fresh air supply should always be available. Leaks in high pressure systems usually result in a flame from the reaction of fluorine with the metal. Shields should be provided for valves, pressure-reducing stations, and gauges. Valves are a particularly susceptible area for fluorine fires that can be initiated by foreign material accumulated at the valve seat. High pressure cylinders and valves should be remotely located with proper personnel protection and the latter should be operated using handle extensions. An excellent guide for the safe handling of fluorine in the laboratory is available (108).

7.1. Toxicity. Fluorine is extremely corrosive and irritating to the skin. Inhalation at even low concentrations irritates the respiratory tract; at high concentrations fluorine inhalation may result in severe lung congestion.

The American Conference of Governmental Industrial Hygienists (ACGIH) has established the 8-hour time-weighted average TLV as 1 ppm or 1.6 mg/m^3, and the short-term exposure limit TLV as 2 ppm or 3.1 mg/m^3. Fluorine has a sharp, penetrating odor detectable at levels well below the TLV. Manifestations of overexposure to fluorine include irritation or burns of the eyes, skin, and respiratory tract. The following emergency exposure limits (EEL) for humans have been suggested (109): 15.0 ppm for 10 min; 10 ppm for 30 min; and 7.5 ppm for 60 min.

Toxicity studies (110–112) established tolerance levels and degrees of irritations, indicating that the eye is the area most sensitive to fluorine. Comprehensive animal studies (113–115) determined a rat LC_{50} value of 3500 ppm · min for a single 5-min exposure and of 5850 ppm · min for a 15-min exposure. A no-effect concentration corresponded to a concentration–time value of ~15% of the LC_{50} levels.

Because of the corrosive effects and discomfort associated with inhalation of fluorine, chronic toxicity does not occur. Although the metabolic fate of fluorine is not clear, it does not seem that much is converted to fluoride ion in the body (109). Therefore comparisons to effects of fluoride ion poisoning, known as fluorosis, are probably incorrect.

7.2. Burns.

Skin burns resulting from contact with pure fluorine gas are comparable to thermal burns and differ considerably from those produced by hydrogen fluoride (116). Fluorine burns heal much more rapidly than hydrofluoric acid burns.

7.3. Disposal.

Fluorine can be disposed of by conversion to gaseous perfluorocarbons or fluoride salts. Because of the long atmospheric lifetimes of gaseous perfluorocarbons (see ATMOSPHERIC MODELING), disposal by conversion to fluoride salts is preferred. The following methods are recommended: scrubbing with caustic solutions (117,118); reaction with solid disposal agents such as alumina, limestone, lime, and soda lime (119,120); and reaction with superheated steam (121). Scrubbing with caustic solution and, for dilute streams, reaction with limestone, are practiced on an industrial scale.

In a caustic scrubbing system, caustic potash, KOH, is preferred to caustic soda, NaOH, because of the higher solubility of the resulting potassium fluoride. Adequate solution contact and residence time must be provided in the scrub tower to ensure complete neutralization of the intermediate oxygen difluoride, OF_2. Gas residence times of at least one minute and caustic concentrations in excess of 5% are recommended to prevent OF_2 emission from the scrub tower.

8. Uses

Elemental fluorine is used captively by most manufacturers for the production of various inorganic fluoride (Table 5). The market for gaseous fluorine in cylinders is small, due to the difficulties involved in handling the gas and the small amount of product that can be packaged into each cylinder. One large use of fluorine is in the manufacture of uranium hexafluoride, UF_6, by

$$UF_4 + F_2 \longrightarrow UF_6$$

Uranium hexafluoride is used in the gaseous diffusion process for the separation and enrichment of uranium-235, which exists in low concentration in natural uranium. The enriched UF_6 is converted back into an oxide and used as fuel for the nuclear power industry.

A large and growing use of fluorine is in the production of nitrogen trifluoride (NF_3). This gas is mainly used for cleaning equipment used in production of electronic components and flat panel displays (see ELECTRONIC MATERIALS; FLUORINE COMPOUNDS, INORGANIC, NITROGEN) Also, NF_3 can be used as a fluorine source in the high power hydrogen fluoride deuterium fluoride (HF/DF) chemical lasers.

Fluorine may be used directly to clean equipment used in the production of computer components (chips) and flat panel displays. For this application two companies offer “on-site” production equipment, Fluorine On Call (Burnet, Texas) and Fluorogas Ltd (divison of the BOC group, United Kingdom). Production capacity of a few kilograms of fluorine gas per hour are possible.

Another large use for elemental fluorine is in production of sulfur hexafluoride, SF_6, a gaseous dielectric for electrical and electronic equipment (see ELECTRONIC MATERIALS; FLUORINE COMPOUNDS, INORGANIC, SULFUR). Its high dielectric strength, inertness, thermal stability, and ease of handling have led to increased use as an electrically insulating medium, permitting reductions in size, weight, and cost of high voltage electrical switch gear, breakers, and substations. Elemental fluorine is also used to produce sulfur tetrafluoride, SF_4, by the reaction of sulfur and fluorine under controlled conditions. Sulfur tetrafluoride is a selective fluorinating agent used to produce fluorochemical intermediates in the pharmaceutical and herbicide industry (see HERBICIDES).

Fluorine reacts with the halogens and antimony to produce several compounds of commercial importance: antimony pentafluoride [7783-70-2], bromine trifluoride [7787-71-5], chlorine trifluoride [7790-91-2], and iodine pentafluoride [7783-66-6]. Chlorine trifluoride is used in the processing of UF_6 (see URANIUM AND URANIUM COMPOUNDS). Bromine trifluoride is used in chemical cutting by the oil well industry (see PETROLEUM). Antimony and iodine pentafluorides are used as selective fluorinating agents to produce fluorochemical intermediates (see FLUORINE COMPOUNDS, INORGANIC).

Fluorination of tungsten and rhenium produces tungsten hexafluoride, WF_6, and rhenium hexafloride [10049-17-9], ReF_6, respectively. These volatile metal fluorides are used in the chemical vapor deposition industry to produce metal coatings and intricately shaped components (see THIN FILMS, FILM FORMATION TECHNIQUES).

Fluorine is used to surface treat polyolefin containers to make them more resistant to permeation by organic liquids. In one application, the air that is normally used to blow-mold containers is replaced by a very dilute concentration of fluorine in a mixture with nitrogen. In another approach, the containers are placed in a large enclosure and subsequently exposed to low concentrations of fluorine-nitrogen, fluorine–carbon dioxide, or fluorine–air mixtures. Containers may vary in size from mascara tubes, small bottles and other containers for cosmetics to automotive fuel tanks, 55-gal (200 L) drums and even 500 gal (2,000 L) tote bins. Fluorine treated plastic containers generally show an outstanding resistance to nonpolar solvents and fuels, sometimes as much as 1000 times greater than untreated containers.

Also fluorine can be used in the preparation of a polymer surface for adhesive (qv) or coatings (qv). In this application the surfaces of a variety of polymers, eg, polyethylene, polypropylene, rubber, polyester, polyurethane, UHMW PE, and aramid, that are difficult or impossible to adhere to are easily and quickly treated to provide surfaces with excellent adhesion. Plastic particles and powders (UHMW PE, HDPE, polypropylene, and others) are treated with fluorine-containing atmospheres to improve dispersion and adhesion properties such that the particles can be used as performance additives in molded goods, paints, coatings, and adhesives. Fluorine surface preparation, unlike wet-chemical surface treatment, does not generate large amounts of hazardous wastes, and has been demonstrated to be much more effective than plasma or corona surface treatments.

Fig. 5. Parts are loaded into large reactor chambers, air is removed via a vacuum pump, and a gas blend containing fluorine in added. Temperature within the chamber can be controlled through jacketing on the reactors. After a predetermined reaction times has elapsed, the chamber is evacuated via a vacuum pump, with effluent gas being neutralized in a caustic scrubber. The chamber is refilled with air, opened, and the surface treated parts are removed.

Furthermore, changes effected by fluorine treatments are generally permanent, which is an advantage over alternative treatment technologies.

Figure 5 illustrates commercial equipment used for surface treating plastic components. Equipment to continuously treat fabrics, fibers, tows, films, sheet foams, and other web materials are also available.

Fluorine is used in the production of fluorinated organics both for the manufacture of perfluorinated materials and for the selective and regiospecific introduction of fluorine. Perfluorinated aliphatics, cycloaliphatics, and polyethers are made by fluorination of the hydrogen-containing analogue using F_2 or CoF_3. The superior chemical and thermal stability of perfluorocarbons has led to uses in high temperature lubrication, thermal testing of electronic components, and as specialty fluids for vacuum pumps, liquid seals, and hydraulic applications. Because of the high solubility of oxygen in these materials, perfluorinated aliphatics and cycloaliphatics have also been used as synthetic blood substitutes (see BLOOD, ARTIFICIAL) (122).

Although the selective introduction of fluorine into biologically important molecules has been demonstrated to provide dramatic improvements in efficacy and toxicity as compared to unfluorinated analogues, commercial methods using fluorine gas are uncommon. A notable exception is the production of 5-fluorouracil, made by the direct reaction of fluorine and uracil, which is used in cancer chemotherapy (see CHEMOTHERAPEUTICS, ANTICANCER). To overcome the difficulties encountered in direct fluorinations, electrophilic fluorinating agents have been commercialized by Honeywell International Inc.; Air Products & Chemicals, Inc.; Daikin Industries Ltd.; and Tosoh FTECH, Inc. These reagents are made from nitrogen-containing compounds, which when reacted with F_2 yield compounds that act as positive fluorine, F^+, sources. The selective introduction of fluorine into many types of organic molecules, including steroids, nucleosides, heterocycles, and aromatic compounds, can be effected using these reagents (55–61).

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