FLUORINE COMPOUNDS, INORGANIC

1. Introduction

Fluorine (qv), the most electronegative element, is much more reactive than the other elements. On the Pauling scale of electronegativities, fluorine (value 4.0) lies well above oxygen (3.5), chlorine (3.0), and nitrogen (3.0) (1). Indeed, fluorine reacts with virtually every other element, including the helium group elements. These last were commonly called inert gases until 1962 when xenon, radon, and krypton were shown to react with fluorine (see HELIUM-GROUP GASES). Because of unique properties, fluorine has been called a superhalogen (1) and several of its compounds called superacids. The term superacid (2) is used for systems having higher acidities than anhydrous sulfuric or fluorosulfuric acid. A number of fluorine species exhibit superacid properties in HSO_3F or HSO_3F-SO_3 solutions. The SbF_5-HSO_3F system is an example.

The basic fluorine-containing minerals are fluorite [14542-23-5], commonly called fluorspar, CaF_2; and fluorapatite [1306-05-4], commonly called phosphate rock. The reaction of calcium fluoride and sulfuric acid produces hydrogen fluoride. Fluorosilicic acid is produced from fluorapatite as a by-product in the production of phosphoric acid. The boiling point of hydrogen fluoride, 19.54°C, is much higher than that of HCl, −84.9°C, owing to extensive molecular association via hydrogen bonding in the former. Hydrogen fluoride is the most common reagent for production of fluorine compounds. The first pure sample of anhydrous hydrogen fluoride was produced from thermal decomposition of KFHF (3,4). Elemental fluorine, a pale greenish yellow gas, is produced by electrolysis of anhydrous potassium fluoride–hydrogen fluoride melts (see also ELECTROCHEMICAL PROCESSING, INORGANIC). IUPAC has recommended the prefix *fluoro* rather than the frequently used *fluo* for inorganic fluorine compounds. Terms such as fluoborate, fluosilicate, and silicofluoride are frequently used, however, rather than the preferred nomenclature, fluoroborate and fluorosilicate.

The fluoride ion is the least polarizable anion. It is small, having a diameter of 0.136 nm, 0.045 nm smaller than the chloride ion. The isoelectronic F^- and O^{2-} ions are the only anions of comparable size to many cations. These anions are about the same size as K^+ and Ba^{2+} and smaller than Rb^+ and Cs^+. The small size of F^- allows for high coordination numbers and leads to different crystal forms and solubilities, and higher bond energies than are evidenced by the other halides. Bonds between fluorine and other elements are strong whereas the fluorine–fluorine bond is much weaker, 158.8 kJ/mol (37.95 kcal/mol), than the chlorine–chlorine bond which is 242.58 kJ/mol (57.98 kcal/mol). This bond weakness relative to the second-row elements is also seen in O–O and N–N single bonds and results from electronic repulsion.

A number of elements exhibit the highest oxidation state only because fluorides and oxidation states of +6 and +7 are not uncommon. Examples of volatile fluorides of high oxidation state include VF_5, CrF_5, TaF_5, WF_6, MoF_6, PtF_6, ReF_6, ReF_7, and IF_7. Many complex fluorides demonstrate coordination not found for the other larger halides, eg, $NiF9_6^{2-}$, SiF_6^{2-}, TaF_7^{2-}, TaF_8^{3-}, PF_6^-, AsF_6^-, ZrF_7^{3-}, and PbF_7^{3-}.

Fluorine forms very reactive halogen fluorides. Reaction of Cl_2 and F_2 at elevated temperatures can produce ClF, ClF_3, or ClF_5; BrF_3 and BrF_5 can be obtained from the reaction of Br_2 and F_2. These halogen fluorides react with all nonmetals, except for the noble gases, N_2, and O_2 (5). Fluorine also forms a class of compounds known as hypofluorites, eg, CF_3OF (6). Fluorine peroxide [7783-44-0], O_2F_2, has also been reported (6).

Fluorine's special properties lead to many applications. Its complexing properties account for its use as a flux in steelmaking and as an intermediate in aluminum manufacture. The reaction of fluorides with hydroxyapatite, $Ca_5(PO_4)_3OH$, which is found in tooth enamel, to form less soluble and/or more acid-resistant compounds, led to the incorporation of fluorides in drinking water and dentifrices (qv) to reduce dental caries. Many fluorides are volatile and in many cases are the most volatile compounds of an element. This property led to the use of UF_6 for uranium isotope enrichment, critical to the nuclear industry (see NUCLEAR REACTORS), and the use of metal fluorides in chemical vapor deposition (WF_6, MoF_6, ReF_6), in ion implantation (qv) for semiconductors (qv) (BF_3, PF_3, AsF_5, etc), and as unreactive dielectrics (SF_6). Because fluorine forms stable bonds, its compounds can be both extremely reactive (F_2, HF, interhalogens, hypofluorides, fluorinated peroxides, ionic MF_x) and extremely stable (CF_4, SF_6, covalent MF_x). Fluorinated steroids, other fluorinated drugs, and anesthetics have medical applications. The stability, lack of reactivity and, therefore, lack of toxicity of some fluorine compounds are also demonstrated by studies reporting survival of animals in an atmosphere of 80% SF_6 and 20% oxygen, and use of perfluorochemicals as short-term blood substitutes because of the ability to efficiently transport oxygen and carbon dioxide (see BLOOD, ARTIFICIAL; FLUORINE COMPOUNDS, ORGANIC). Fluorides including HF, BF_3, SbF_5, PF_5, and several complexes, eg, BF_4^-, PF_6^-, SbF_6^-, and AsF_6^-, are used in many applications in catalysis (qv).

2. History

The names fluorine and fluorospar are derived from the Latin *fluere* meaning flow or flux. In 1529 the use of fluorspar as a flux was described. In 1670 the etching of glass by acid-treated fluorspar was reported. Elemental fluorine was isolated by Moissan in 1886 (7).

Fluorspar has been used as a flux in the steel industry since the introduction of the open-hearth process. Historically, hydrogen fluoride was used in limited quantities for glass etching, polishing, scale removal, and small-volume production of fluorides. In the 1930s the first significant commercial HF production was applied toward the production of aluminum (see ALUMINUM AND ALUMINUM ALLOYS) and chlorofluorohydrocarbons for refrigerants (see REFRIGERATION AND REFRIGERANTS). During World War II HF was used in alkylation catalysis to produce aviation gasoline and in the manufacture of fluorine to produce volatile UF_6 for isotopic enrichment of the uranium essential for nuclear devices. The use of the very corrosive UF_6 also stimulated development of fluorinated organic compounds for lubricants and seals that are resistant to UF_6 (see LUBRICATION AND LUBRICANTS). Anhydrous HF is used both as a reactant and as a solvent (4) in the manufacture of inorganic fluorides.

3. Sources and Applications

The earth's crust consists of 0.09% fluorine. Among the elements fluorine ranks about thirteenth in terrestrial abundance.

The ores of most importance are fluorspar, CaF_2; fluorapatite, $Ca_5(PO_4)_3F$; and cryolite [15096-52-3], Na_3AlF_6. Fluorspar is the primary commercial source of fluorine. Twenty-six percent of the world's high quality deposits of fluorspar are in North America. Most of that is in Mexico. United States production in 1987–1991 was 314,500 metric tons, most of which occurred in the Illinois–Kentucky area. Imported fluorspar in 1990–1991 represented about 82% of U.S. consumption; 31% of U.S. fluorspar imports were from Mexico and 29% from China compared to 66% from Mexico in the 1973–1978 period. The majority of the fluorine in the earth's crust is in phosphate rock in the form of fluorapatite which has an average fluorine concentration of 3.5%. Recovery of these fluorine values as by-product fluorosilicic acid from phosphate production has grown steadily, partially because of environmental requirements (see PHOSPHORIC ACID AND THE PHOSPHATES).

Production of hydrogen fluoride from reaction of CaF_2 with sulfuric acid is the largest user of fluorspar and accounts for approximately 60–65% of total U.S. consumption. The principal uses of hydrogen fluoride are in the manufacture of aluminum fluoride and synthetic cryolite for the Hall aluminum process and fluoropolymers and chlorofluorocarbons that are used as refrigerants, solvents, aerosols (qv), and in plastics. Because of the concern that chlorofluorocarbons cause upper atmosphere ozone depletion, these compounds are being replaced by hydrochlorofluorocarbons and hydrofluorocarbons. The balance of hydrogen fluoride is used in applications such as stainless steel pickling, inorganic fluoride production, alkylation (qv), uranium enrichment, and fluorine production. Hydrogen fluoride is used to convert uranium oxide to UF_4 which then reacts with elemental fluorine to produce volatile UF_6. The UF_6 is then isotopically enriched by gaseous diffusion or gas centrifuge processes for nuclear applications.

The steel (qv) industry is also an extremely large user of fluorspar which is added to slag to make it more reactive. Smaller amounts are also used in the aluminum, ceramic, brick, cement, glass fiber, and foundry industries.

4. Synthesis

Most inorganic fluorides are prepared by the reaction of hydrofluoric acid with oxides, carbonates, hydroxides, chlorides, or metals. Routes starting with carbonate, hydroxide, or oxide are the most common and the choice is determined by the most economical starting material. In many cases, the water produced by the reaction cannot be removed without at least partial hydrolysis of the metal fluoride. This hydrolysis frequently can be reduced by dehydrating in a stream of hydrogen fluoride. If hydrolysis is unavoidable, reaction of anhydrous HF and the metal or the metal chloride may be required. The reaction of the metal and HF can be the most desirable if the metal is inexpensive relative to its salts and if the metal has an oxidation potential higher than hydrogen. If the metal is not finely divided, formation of a fluoride coating on the metal surface may occur. This may slow the reaction. Another route to metal fluorides is by reaction of the metal or its salts with elemental fluorine or with interhalogen fluorides. These reactions occur rapidly and frequently are violent. Because hydrofluoric acid is much less expensive than fluorine, it normally is used whenever possible. However, many of the compounds containing elements in the higher oxidation states can be achieved only by use of elemental fluorine.

5. Analysis and Characterization

The most popular device for fluoride analysis is the ion-selective electrode (see ELECTROANALYTICAL TECHNIQUES). Analysis using the electrode is rapid and this is especially useful for dilute solutions and water analysis. Because the electrode responds only to free fluoride ion, care must be taken to convert complexed fluoride ions to free fluoride to obtain the total fluoride value (8). The fluoride electrode also can be used as an end point detector in titration of fluoride using lanthanum nitrate [10099-59-9]. Often volumetric analysis by titration with thorium nitrate [13823-29-5] or lanthanum nitrate is the method of choice. The fluoride is preferably steam distilled from perchloric or sulfuric acid to prevent interference (9,10). Fusion with a sodium carbonate–sodium hydroxide mixture or sodium may be required if the samples are covalent or insoluble.

Because fluorine has a nuclear spin of one-half, a strong signal, and a large coupling constant, nmr spectroscopic analysis is an invaluable tool (see MAGNETIC SPIN RESONANCE). The use of gas chromatography on the many volatile fluorine compounds also has greatly enhanced separation and identification. However, nuclear magnetic resonance and infrared spectroscopy remain key techniques in the study of fluorine compounds (see INFRARED AND RAMAN SPECTROSCOPY). Raman spectroscopy and mass spectrometry (qv) are also useful tools.

6. Safety, Toxicity, and Handling

Hazards associated with fluorides are severe. Anhydrous or aqueous hydrogen fluoride is extremely corrosive to skin, eyes, mucous membranes, and lungs; it can cause permanent damage and even death. Detailed information about safety, toxicity, and handling can be obtained from the producers of hydrogen fluoride, eg, Elf Atochem North America, Inc., Du Pont, and AlliedSignal. Fluorides susceptible to hydrolysis can generate aqueous hydrogen fluoride. Ingestion of excess fluorides may cause poisoning or damage to bones and/or teeth. Fluorine-containing oxidizers can react with the body in addition to causing burns.

Hydrogen fluoride or compounds that can produce it and fluorine-containing oxidizers should be handled with adequate safety equipment and extreme care by well-trained personnel. Often the effect of skin exposure is not immediately evident, especially when dilute solutions are handled. Pain may develop several hours later.

Fluorides in small (1 ppm in water, 0.1% in dentifrices) quantities have been shown to provide dramatic reduction in dental decay. Fluorides also show promise for bone treatment and in pharmaceuticals (qv) (see also CHEMOTHERAPEUTICS, ANTICANCER; STEROIDS). However, larger quantities of fluorides can lead to dental fluorosis,bone fracture, and even death. The oral LD_{50} for free fluoride ion in rats appears to be 50 to 100 mg/kg body weight based on LD_{50} values for several fluorides.

Because hydrogen fluoride is extremely reactive, special materials are necessary for its handling and storage. Glass reacts with HF to produce SiF_4 which leads to pressure buildup and potential ruptures. Anhydrous hydrogen fluoride is produced and stored in mild steel equipment. Teflon or polyethylene are frequently used for aqueous solutions.

The OSHA permissible exposure limit (11) and the American Conference of Governmental Industrial Hygienists (ACGIH) established threshold limit value (TLV) (12) for fluorides is 2.5 mg of fluoride per cubic meter of air. This is the TLV–TWA concentration for a normal 8-h work day and a 40-h work week.

BIBLIOGRAPHY

"Fluorine Compounds, Inorganic," in *ECT* 1st ed., Vol. 6, pp. 667–668, by C. R. Hough, Polytechnic Institute of Brooklyn; in *ECT* 2nd ed., Vol. 9, pp. 527–529, by J. B. Beal, Jr., Ozark-Mahoning Co.; in *ECT* 3rd ed., Vol. 10, pp. 655–659, by C. B. Lindahl and D. T. Meshri, Ozark-Mahoning Co.; in *ECT* 4th ed., Vol. 11, pp. 267–273, by Charles B. Lindahl and Tariq Mahmood, Elf Atochem North America, Inc.

CITED PUBLICATIONS

1. L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, pp. 82 and 90.
2. R. J. Gillespie, *Acc. Chem. Res.* **1**, 202 (1968).
3. E. F¢my, *Ann. Chim. Phys.* **47**, 5 (1856).
4. R. E. Banks, *J. Fluorine Chem.* **33**, 3–26 (1986).
5. O. Glemser, *J. Fluorine Chem.* **33**, 45–69 (1986).
6. J. M. Shreeve, *J. Fluorine Chem.* **33**, 179–193 (1986).
7. H. Moissan, *Compt. Rend.* **12**, 1543 (1886).
8. *Analytical Procedures for Fluoride Analyses*, Orion Research Inc., Boston, Mass., 1990–1991.
9. G. H. Cady, *Anal. Chem.* **48**, 655–660 (1976).
10. H. H. Willard and O. B. Winter, *Ind. Eng. Chem. Analyt. Edn.* **5**, 7–10 (1933).
11. *Code of Federal Regulations*, Title 29, Part 1910.1000, Washington, D.C.
12. *Threshold Limit Values for Chemical Substances and Physical Agents, 1992–1993*, The American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio.

GENERAL REFERENCES

Chemistry and characteristics P. Tarrant, ed., *Fluorine Chemistry Reviews*, Vol. 6, Marcel Dekker Inc., New York, 1971; Vol. 1, 1967; Vol. 2, 1968; Vol. 3, 1969; Vol. 4, 1969; Vol. 5, 1973; Vol. 7, 1974; Vol. 8, 1977.

J. H. Simons, ed., *Fluorine Chemistry*, Academic Press, Inc., New York, Vol. 1, 1950; Vol. 2, 1954; Vol. 3, 1963; Vol. 4, 1965; Vol. 5, 1964.

M. Stacey and co-eds., *Advances in Fluorine Chemistry*, Butterworth Inc., Washington, D.C., Vol. 1, 1960; Vol. 2, 1961; Vol. 3, 1963; Vol. 4, 1965; Vol. 5, 1965; Vol. 6, 1970; Vol. 7, 1973.

G. Brauer, *Handbuch der Praparativen Anorganischen Chemie*, Ferdinand Enke, Stuttgart, Band 1, 1960; Band 2, 1962.

I. G. Ryss, *The Chemistry of Fluorine and Its Inorganic Compounds*, State Publishing House of Scientific, Technical, and Chemical Literature, Moscow, 1956; Eng. trans., AEC-tr-3927, Office of Technical Services, U.S. Dept. of Commerce, Washington D.C., 1960.

F. A. Cotton, ed., *Progress in Inorganic Chemistry*, Vol. 2, Interscience Publishers, Inc., New York, 1960.

Mellor's Comprehensive Treatise of Inorganic and Theoretical Chemistry, Vol. 2, Suppl. 1, Longmans Green & Co. Ltd., London, 1962.

Gmelin, *Handbuch der Anorganischen Chemie*, Fluorination System-Number 5, Verlag Chemie, GmbH, Weinheim, Germany, 1959.

M. F. A. Dove and A. F. Clifford, *Inorganic Chemistry in Liquid Hydrogen Fluoride*, Pergamon Press Ltd., Oxford, U.K., 1971.

E. Newbrun, ed., *Fluorides and Dental Caries*, Charles C Thomas Publishers, Springfield, Ill., 1975.

W. E. Jones and E. G. Skolnik, *Chem. Rev.* **76**, 563 (1976).

R. E. Banks, D. W. A. Sharp, and J. C. Tatlow, eds., *Fluorine, The First Hundred Years*, Elsevier, Science Publishing Co., Inc., New York, 1986, and *Journal of Fluorine Chemistry*, Vol. 33.

Production, consumption, uses, prices, and imports

Minerals Yearbooks Chapter on Fluorspar (annual comprehensive reports but delayed approximately two years).

Mineral Industry Surveys on Fluorspar, quarterly, and annual (less comprehensive but current).

U.S. Dept. of the Interior, Bureau of Mines, Washington, D.C. (periodic).

CHARLES B. LINDAHL
TARIQ MAHMOOD
Elf Atochem North America, Inc.