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Considering the long time in which fluorine compounds have been used it seems rather surprising that it was not isolated as an element until 1886. This long delay was not due to lack of effort, but to the reactivity of fluorine and the hazards of working with it and many of its compounds.

History (*1–3*)

Georgius Agricola in 1529 discussed the use of a mineral, fluores, to reduce the melting point of various ores. This lowering of the melting point saved much time and fuel during the smelting process. The name fluores was from the Latin, *fluere* (to flow), alluding to its ability to help the ore to liquify or flow. The name was later changed to fluorspar, and then to fluorite so that its name would conform to standard mineral terminology. Fluorite is still being used in the steel making process. The composition of fluorite is CaF_2.

In 1670 the use of another fluorine compound was initiated. Heinrich Schwanhard of Nuremburg discovered that when a strong acid was added to fluorite, a gas evolved that etched the glasses he was wearing. Since he was a member of a famous family of glass cutters, he quickly realized the commercial potential of this process, and became very successful producing art figures by etching glass. This process was kept a trade secret for many years.

Carl Scheele, a Swedish chemist, in 1780 determined that the gas generated by Schwanhard's process was an acid. He called this acid "fluoric acid." Scheele had a habit of smelling and tasting all of the new chemicals that he isolated. This habit, no doubt, contributed to his early death.

In 1810, chlorine was discovered. It was the first halogen to be isolated and recognized as an element. Chlorine was prepared by Sir Humphry Davy by oxidizing muriatic (hydrochloric) acid. Davy then went on to show that fluoric acid was analogous to hydrochloric acid. André Ampère and Davy then assumed that an element analogous to chlorine existed in this acid. They named the new element fluorine (from the root of fluorite). Fluorite was determined to be calcium fluoride. The next step was to isolate this new element. The obvious way to isolate fluorine was by a method similiar to that used to isolate chlorine. However, it was found that the acid, now called hydrofluoric acid, could not be oxidized. This result would seem obvious today because it is well known that fluorine is the most electronegative element, and therefore, the fluoride ion is the most difficult to oxidize.

At about this time it was found that compounds could be broken down by electricity. Davy was able to isolate several elements this way, but when he attempted to produce fluorine by the electrolysis of fluorite, he was unsuccessful. The probable reason for this failure was that any fluorine formed would immediately react with anything it came in contact with at the temperature at which fluorite is a liquid. During this work Davy was poisoned by hydrogen fluoride and suffered from its effects for many years.

During most of the remainder of the nineteenth century several attempts to isolate fluorine were made. The results of these efforts were the early deaths of George Knox, P. Louyet, and Jérôme Nicklès, and a close brush with death for Thomas Knox (George's brother).

In 1885 the French scientist Edmond Frémy, one of Louyet's assistants, took up the challenge of isolating fluorine. After repeating Davy's work with no success, he decided to try the electrolysis of hydrogen fluoride since this could be done at a much lower temperature than the electrolysis of calcium fluoride. His early results showed that oxygen appeared at the anode instead of fluorine. This was apparently due to the presence of water in the hydrogen fluoride. Frémy then set about preparing anhydrous hydrogen fluoride. He succeeded in this task, but a new problem arose: anhydrous hydrogen fluoride did not conduct electricity, so it could not be electrolyzed.

One of Frémy's students, Ferdinand Frédéric Henri Moissan, continued the work. After several false starts he was able to isolate a pale yellow-green gas on June 26, 1886. At this time Moissan tried the electrolysis of anhydrous hydrogen fluoride obtained by distillation from a potassium bifluoride melt. This work was carried out using platinum or platinum alloy apparatus. However, even the inert platinum was attacked so that the weight loss of the platinum was greater than the weight of fluorine produced. When Moissan attempted to repeat this experiment in front of a committee appointed by the Académie des Sciences, he was unsuccessful. Following this he discovered that the reason why his original experiment worked was that his hydrogen fluoride had been contaminated by a little potassium fluoride. He had redistilled the hydrogen fluoride before the demonstration for the committee, and the impurity was removed so it would not conduct electricity. Moissan continued his work with fluorine, and improved his techniques. His successful work in isolating elemental fluorine led to his receipt of the Nobel Prize in 1906.

While it was now possible to prepare fluorine, it would be many years before it would be possible to routinely work with it in the laboratory or in industry.

Preparation

In 1899, Moissan modified his original method of preparation by substituting copper for the more expensive platinum. Copper is attacked by fluorine also, however a coating of copper (II) fluoride forms that protects the copper from further attack. Over the years the electrolyte has been modified in various ways. The currently used composition has approximately a 2:1 ratio of HF to KF (*4*). As the electrolysis cell is operated, anhydrous hydrogen fluoride is added to keep the electrolyte composition relatively constant.

During the first half of this century several chemists, most notably Otto Ruff, attempted to find a reagent that could be used to produce elemental fluorine by a chemical reaction. They were only partially successful. While compounds were found that would decompose to yield fluorine, all of these compounds required elemental fluorine in their synthesis.

The structure, properties, and uses of a variety of chemicals are highlighted in this feature which is aimed at increasing the use of descriptive chemistry.

There is now a system that will produce elemental fluorine chemically. It is

$$UCl_5 + 5\,HF \rightarrow UF_5 + 5\,HCl$$

$$2\,UF_5 \rightarrow UF_4 + UF_6$$

$$UF_6 + 2\,KF \rightarrow K_2UF_8$$

$$3\,K_2UF_8 \rightarrow 2\,K_3UF_8 + UF_6 + F_2$$

This series will probably not be commercially useful, but it is interesting to note that after so many years it is now possible to produce fluorine chemically (5–8).

Occurance

Approximately 170 minerals are known that contain some fluorine. However, only two of these, fluorite (CaF_2) and apatite ($Ca_5(PO_4)_3(F,OH,Cl,\frac{1}{2}CO_3)$), occur widely. Another mineral, cryolite (Na_3AlF_6), is used in aluminum refining and so is very important, but it is only found in four or five places in the world. Only one place, Ivigtut, Greenland, has any significant amounts. In many of the minerals containing fluorine, the fluoride ion replaces the hydroxide ion, therefore all hydroxide species may contain varying amounts of fluorine. This replacement is due to the similarity in size and charge between these two ions.

Fluorite is a very widespread mineral, and it is mined in many places. As mentioned earlier it is still being used as a flux in the steel industry. Some varieties of fluorite contain small amounts of rare earth metals. The term fluorescense came about because it was first discovered in specimens of fluorite. Fluorescence is a relatively common phenomenon in fluorite ores.

Apatite is a major source of phosphate for fertilizer. There are many types of apatite depending on whether fluoride, chloride, hydroxide, or carbonate is the primary anion in addition to phosphate. At present, fluorine from fluorapatite (the fluorine-rich apatite) is not being exploited commercially.

Physical Properties (*9–13*)

Fluorine is a pale yellow diatomic gas and it is the lightest member of the halogen family. It is too reactive to occur naturally in its elemental state. It is the thirteenth most abundant element in the earth's crust, making up 0.065%. Fluorine has only one stable isotope, ^{19}F. One other isotope, ^{18}F, has been used in some tracer studies, however its half-life (109.5 ± 0.5 minutes) is too short for many radioisotope studies.

Fluorine has an atomic weight of 18.998403. Its melting point is 53.54 K and its boiling point is 85.02 ± 0.02 K. The gas has an ionization energy of 402 kcal/mole and an electron affinity of 81 kcal/mole. Fluorine has a standard reduction potential of +2.9 V. It is also the most electronegative of all elements (4.10 Allred-Rochow Scale, 3.98 Pauling Scale, 3.91 Milliken Scale). The covalent radius is 71 pm and the ionic radius of an octahedrally coordinated fluoride ion is 133 pm. The enthalpy of dissociation is 37.7 ± 0.1 kcal/mole.

Chemical Properties

Fluorine will react vigorously with most oxidizable substances. It will also react with many materials normally thought to be stable. Thus materials like water, glass, and asbestos may burn in fluorine. The products from the reaction with water are: HF, OF_2, H_2O_2, O_2, and O_3. Fluorine reacts with nitric acid and sulfuric acid to form NO_3F and $HFSO_3$, respectively. Any fuel (i.e., hydrocarbon or hydrogen) or any organic substance will react explosively with fluorine. The reaction with hydrogen does not need to be photoinitiated as does the reaction of hydrogen with chlorine.

The high electronegativety of fluorine enables it to have some special chemical properties. This electronegativity allows it to withdraw electrons from cations that are not formed by other oxidizing agents. This results in some unusual oxidation states. Examples of these are compounds containing species such as O^{+2}, Cu^{+4}, Ag^{+5}, and Au^{+5}. On the other hand, it does not stabilize low oxidation states, thus copper (I) fluoride disproportionates to copper (II) fluoride and copper.

Another special property of fluorine is that it has been found to be able to form compounds with the noble gases. It is the only element that will react directly with a noble gas.

In general, most of the chemical properties of fluorine resemble those of the other halogens. The major difference is the energetics involved. These energetics are, in part, due to the electron affinity of fluorine (even though it is lower than that of chlorine), in part due to the low bond dissociation energy of diatomic fluorine, and in part due to the strengths of the bonds it forms with other elements. Bonds in fluorides are, in general, stronger than bonds in compounds containing other anions.

Uses

The first time elemental fluorine was used on a large scale was during World War II. A method was needed for separating fissionable ^{235}U from the more abundant ^{238}U. It was found that uranium (IV) oxide, from uranium ores, could be reacted with anhydrous hydrogen fluoride to produce uranium (IV) fluoride which could, in turn, be converted to the hexafluoride when reacted with fluorine gas. When uranium (VI) fluoride is heated to 56°C it sublimes, and the $^{235}UF_6$ and $^{238}UF_6$ can be separated by vapor diffusion. The research and development required to make this process operational greatly advanced fluorine technology so that many more processes requiring elemental fluorine became feasible, both in the laboratory and in industry.

Elemental fluorine is now also used to make sulfur hexafluoride by the direct combination of the elements. This compound is a gaseous insulator with a high dielectric constant. It is thermally stable and may be handled easily. Sulfur hexafluoride has been used as an insulator in electronics equipment as well as a dielectric in x-ray tubes.

Fluorine, or one of its derivatives such as chlorine trifluoride or oxygen difluoride (both are nearly as reactive), may become important as an oxidizing agent in rocket propulsion. The potential value lies in the fact that reactions between various fuels and these compounds have a high specific impulse. Propulsion systems employing these compounds will probably become widely used if the storage and handling problems involved can be overcome. Since the reaction of any of these oxidants with materials containing hydrogen will yield hydrogen fluoride, it is unlikely that they will be used in the earth's atmosphere.

Several fluorine compounds developed on a wide scale since World War II have developed great industrial importance. One of these, polytetrafluoroethylene (Teflon®, Fluon®), is known for its chemical inertness and its low frictional properties. It is nonflammable and has no known solvents. These properties make it valuable for tubing, non-stick surfaces, experimental equipment, and many other uses.

Several low-boiling chlorofluorocarbons, known as freons, are also important. These compounds have found wide usage in cooling and refrigeration units. In the past they were also used extensively as propellants in aerosols, but this has been curtailed due to environmental factors. It might be noted that the effects on the earth's ozone layer are due to the chlorine present in these compounds. The extreme stability of most fluorides do not allow the fluorine to become involved in free radical mechanisms such as those proposed for chlorine.

Other industrially important fluorine compounds include cryolite and fluorite mentioned above and hydrogen fluoride. Hydrogen fluoride has many uses including its use as a solvent and as a catalyst in the petroleum industry.

Biological Aspects (*14, 15*)

Fluorine has the honor of being employed in some of the least toxic compounds as well as being employed in some of the most toxic known compounds. Elemental fluorine itself is very toxic. The recommended maximum exposure to elemental fluorine is 0.1 ppm.

Fluoride poisoning may be either acute or chronic. The ingestion of 5–10 g of sodium fluoride has been estimated to be the "certainly lethal dose" for a 70 kg man. Recovery from a non-lethal dose is rapid. Treatment normally involves calcium therapy which ties the fluoride up as calcium fluoride and restores the calcium levels in the body.

Chronic poisoning is known as fluorosis. It results from the ingestion of 20–80 mg daily over a period of several years. The symptoms are usually skeletal abnormalities or damage. These may range from stiffness to permanent skeletal rigidity.

The addition of fluoride to drinking water (~1 ppm) has been shown to reduce dental caries. The fluoride ion replaces hydroxide ion in the teeth to produce fluorapatite which is more resistant to acid attack by bacteria. In addition, the fluoride ion has germicidal characteristics. Higher levels of fluoride ion cause a brown staining in addition to the beneficial aspects of fluoridation. There has been no substantiated determination that a 1 ppm fluoride ion concentration in drinking water is harmful in any way.

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