Studies on Fluorine at Low Temperatures. I. Preparation, Analysis and Handling of Fluorine.

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General Introduction. Although fluorine is as abundant in nature as many other ordinary elements, no great progress has yet been made in the study of its physical or chemical properties. This is probably due to the fact that its chemical property is so violent that it can be handled with great difficulty and accordingly its use has not yet been well known.

Studies on fluorine have so far been made chiefly by (i) Moissan and Dewar. Moissan discovered fluorine in the form of element in 1886. Since then he carried out various qualitative investigations, and in collaboration with Dewar, went so far as liquefying and solidifying it, thus accomplishing preliminary studies on fluorine at low temperatures by the beginning of this century.

His studies went far ahead of his age, but no further study has since been made on the properties of fluorine at low temperatures. This is the reason why the somewhat inaccurate results of his studies are still in use. For instance, the melting point of fluorine has been given as −223°C. or −233°C. in several papers(1) since Moissan and Dewar(2) reported that "the melting point of fluorine was a little higher than that of oxygen—it was 40°K. or about −223°C." (The melting point of oxygen is now regarded as −219°C.)(3)

(ii) Ruff and his followers. Ruff carried out investigations for obtaining chemical compounds of fluorine and other halogens or oxygen, nitrogen, carbon, etc. As a result of his painstaking investigations extending over more than a quarter of a century, he took initiative in producing almost all new gaseous compounds of fluorine, the number of his papers published on such compounds coming to about 30. Ruff's investigations, however, were intended for producing new compounds, the chemical kinetics of the reactions concerned or various properties of the products of the reactions generally being left out of consideration.

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(1) "International Critical Table"; Landolt and Börnstein, "Physikalisch-chemische Tabellen"; Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II; Henglein, *Z. anorg. allgem. Chem.*, **118** (1921), 165.

(2) Moissan and Dewar, *Compt. rend.*, **136** (1903), 641.

(3) Clusius, *Z. physik. Chem.*, B, **3** (1929), 41.

(iii) Simmon, Cady, Schumacher, and others. They are making studies on oxides of fluorine and organic compounds of fluorine. A few others are making researches on the compounds of fluorine.

In short, investigations of fluorine are lagging far behind those of other elements and compounds, and enumeration of all the books and papers on the studies of fluorine would not be very difficult.

The boiling point and melting point of this element are as low as −188°C. and about −220°C. respectively. It resembles oxygen in this respect. The characteristics of permanent gases, such as oxygen, nitrogen, hydrogen, etc. in their liquid and solid states have been examined from every point, while those of fluorine alone have been left almost untouched. Further, fluorine shows chemical reaction even at a very low temperature, which is not the case with other elements, and for this reason, the study of this element at low temperatures was the more interesting and valuable. The experiments on fluorine at low temperatures were technically easier than at ordinary temperature, as it becomes somewhat less corrosive to the apparatus and material used. But it was found that the results of investigations so far made on the characteristics of fluorine itself were so unreliable that no experiment or theoretical studies could be carried out with confidence on the basis of these results. The authors first intended to make clear the various characteristics of fluorine at low temperatures. In the following papers are given the results of the studies on fluorine gas at low temperatures and on liquid and solid fluorine.

On account of the chemical activity, the preparation, analysis, and experiment of this element are attended with many technical difficulties. But owing to the improvements in the apparatus and in the materials as well as to the valuable experiences of former investigators in this field, the present authors are now in a position to make experiments for not only qualitative but also quantitative determination of some properties of fluorine. Our first paper deals with the preparation of fluorine and a few experiences in handling fluorine.

I. Preparation of Fluorine. Fluorine was prepared by electrolysis of molten potassium bi-fluoride ($KF \cdot HF$). There are several papers referring to such a method of preparing fluorine.(4) The authors use improved Dennis's V-shaped electrolyser.

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(4) Argo, Mathers, and Humiston, *J. Phys. Chem.*, **23** (1919), 348; Simon, *J. Am. Chem. Soc.*, **46** (1924), 2175; Lebeau, *Compt. rend.*, **181** (1925), 915; Ishikawa, *Bull. nst. Phys. Chem. Research* (Tokyo), **10** (1931), 176; Dennis, *J. Am. Chem. Soc.*, **53** (1931), 3236; Miller and Bigelow, *ibid.*, **58** (1936), 1585.

(1) *Electrolyser*. As shown in Fig. 1, copper pipes 60 mm. in outside diameter, 50 mm. in inside diameter, and 35 cm. in length are brazed into a V-shaped pipe, and a tube to hold the thermometer is also brazed at the joint.

The caps are of flange type, and lead rings are used as the gasket for making the contact between the caps and the pipes gas-tight. In the centre of the flanges there are hollow spots for keeping cement with which the electrodes are fixed to the caps. The electrodes are of ordinary Acheson graphite, 12 mm. in diameter. But, as the rods are slender and too fragile, about one third of their total length is replaced by copper rods, into which the graphite is inserted. The joints are fastened with belts as represented by b in the figure. In this way the fixing of the electrodes with cement at a becomes easy. For preventing the electrodes from loosening at a and for fixing them firmly, the copper rods are fitted with iron nails. Further, molten potassium hydrogen fluoride was spread over the cement when the gas-tightness with cement alone became imperfect in the course of use of the apparatus. A nichrome wire is wound around the vessel pipe for heating. The exit c for the gas produced is made as wide as possible. If it is narrow, the vaporized fluoride will condense here while the vessel is being used, and will choke the exit. The cell was charged with one kg. of Merck's potassium bi-fluoride, which was melted at 230–240°C.

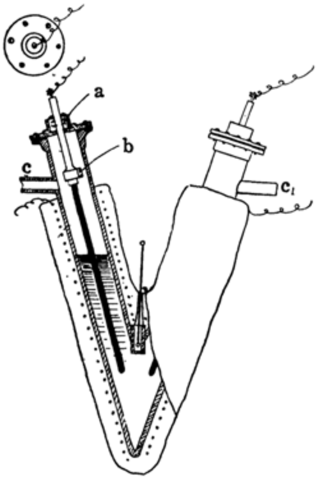

Fig. 1.

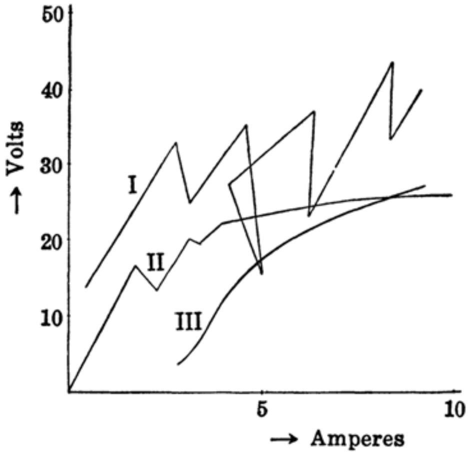

Fig. 2. I: Nondehydrated salt.
II: Dehydrated salt.
III: Salt dehydrated and subjected to a few hours' electrolysis.

(2) *Electrolysis and drying of salt.* The salt began to melt at about 240°C. according to the thermometer in the middle of the arms of the cell. As the fresh salt contained much water, oxygen alone was produced on electrolysis. After this process was continued for a certain time, fluorine was produced. Until this time, the voltage and the current between the two poles varied much (Fig. 2), discharge occurred between the anode and the molten salt, the graphite pole was broken, and the salt became very dirty. There was also a fear of explosive production of the gas. It was therefore necessary to dehydrate perfectly the salt before electrolysis.

To dry the salt, the flange-shaped caps holding the electrodes were replaced by caps having an opening for the gas, by which the tube was connected with a gas-circulating device with a desiccator of phosphorus pentoxide. Air was circulated for 24 hours through the salt kept at 230–240°C. After this treatment, fluorine was produced smoothly as soon as the current ran. The electrolysis was effected at about 5 amp., 15 volts, 240–250°C. in the early stage and at 270–280°C. when hydrogen fluoride in the salt became scanty after several hours. The salt was renewed in about 200 ampere-hours.

The gas produced during a given time with a current kept constant at 5 amp. was led into an aqueous solution of potassium iodide, and the amount of fluorine was determined by iodometry. The efficiency of current was 75–90%, varying with aging of the salt.

(3) *Purity of fluorine.* For the quantitative determination of fluorine, iodometry using an aqueous solution of potassium iodide was carried out, while for examination of the purity of the gas produced, the following method was adopted in view of the fact that mercury acts on fluorine quantitatively to form mercury fluoride.

A Pyrex glass bulb was filled with the sample of fluorine with the addition of a small quantity of mercury, and was shaken. Then the bulb was connected with a mercury pressure gauge and the pressure of the remaining gas was examined.

Naturally, the purity of fluorine varied also according to the time lapse in the electrolysis. The following figures were obtained from a salt dried for 24 hours: F_2 97%, O_2 2.5% after 5 hours' electrolysis; F_2 99.8% after 20 hours' electrolysis. There were other impurities such as CF_4, O_3, Cl_2, HF, etc.

(4) *Purification and storing of fluorine.* The above-mentioned impurities in fluorine decrease with aging of the salt, only hydrogen fluoride remains in the same quantity. Hydrogen fluoride can be eliminated by

passing the gas over powdered sodium fluoride. Other impurities and a trace of hydrogen fluoride are solidified in a trap cooled by liquid oxygen (the boiling point of fluorine is about −188°C. and that of oxygen −183°C.).

Fluorine perfectly dried and freed from hydrogen fluoride is not very corrosive to glass. If it is to be kept in a glass bulb, however, an extremely large volume is needed. Moreover, it will attack glass to some extent at ordinary temperature. On this account, it is desirable to keep it in the liquid state in a trap cooled by liquid nitrogen.

II. Some Techniques of Experiments on Fluorine. (1) *Materials for the apparatus.* The progress of chemical and physical researches on fluorine has been greatly hindered by the highly corrosive nature of fluorine and the difficulties in manufacture of the apparatus. The following is the summary of the authors' experiences gained from the studies in this field.

(i) Fluorine is far less corrosive when it does not contain any trace of hydrogen fluoride nor any moisture than when it does.

(ii) Hard glass is of course preferable to ordinary glass, while Pyrex glass is better than hard glass.

(iii) Quartz is a little more anti-corrosive than glass. But the life of a quartz film pressure gauge and the like which are used for other corrosive gases (such as chlorine) becomes very short when used for fluorine at ordinary temperature.

(iv) Apparatus made of anti-corrosive metals are more durable than those made of glass. According to the results of tests on the exposure of various metal pieces to fluorine, platinum, gold, magnesium, nickel, monel-metal, and copper are anti-corrosive. Of these metals, magnesium and the others that follow form a very tight anti-corrosive film. Especially, the fluoride film on magnesium is generally expected to serve for an anti-corrosive agent when this metal is used for industrial purposes, because the film is very tight and insoluble in water. In workability, copper and monel-metal are the best for the apparatus. Platinum filament (about 0.1 mm. in diameter), when used in fluorine for heating it, formed platinum fluoride at about 400°C., emitting yellow smoke. Ordinary solder may be used at ordinary temperature. Lead plates were used as the gasket of the electrolyser. This gasket, which was heated to about 150°C., could be kept gas-tight, but it had to be renewed at times.

(v) Gas-tight materials. Of course D'kotinsky cement and pitches cannot be used in the experiment on fluorine. For keeping the apparatus proof against fluorine gas, the following substances may be used for the packing or coating for the joint in the apparatus: (a) molten potassium fluoride; (b) molten potassium hydrogen fluoride; (c) plaster, lead oxide, and the like as kneaded with glycerine; (d) further, as both gas-tight and insulating material may be used bakelite which has been properly heat-treated.

(vi) Lubricating materials. Grease naturally burns when it is used as lubricating material on the ground glass surface of a glass cock. Even very hard grease, though it did not burn when the cock was turned off and fluorine remained still in a glass vessel, burst into blue flame every time when the cock was turned and fluorine was streaming. Accordingly a paste of glycerine or of phosphoric acid was used. Even such a material, however, can not be used for a long time. In the experiment in which gas-tightness was required, an anti-corrosive metal valve as shown in Fig. 3 was used.

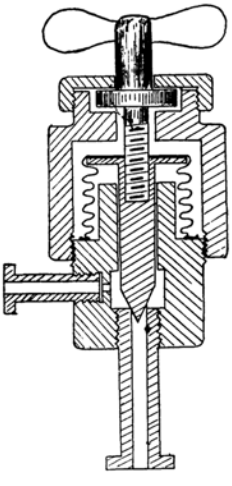

Fig. 3.

(2) *Vacuum cocks.* Since Bodenstein devised a metal valve, a number of similar kinds have been worked out. The present authors used a valve as shown in Fig. 3. In this valve, the ground metal surface can be renewed and a corrugated copper tube is used. Its construction and function will be understood by the section diagram in Fig. 3.

(3) *Mercury.* As stationary mercury makes a tight fluorine film, it may be used for hermetically sealing a joint between ground glass surfaces. If used in a mercury pressure gauge, it must not be in direct contact with fluorine. A quartz film pressure gauge or a platinum film pressure gauge may be used for fluorine. (See the paper on the determination of vapour pressure.)

In rough determination of the pressure, mercury with glycerine placed on it may be used.

III. Reaction between Fluorine and Inflammable Solids at Ordinary Temperature. According to Moissan, fluorine burns various elements such as carbon, sulphur, phosphorus, silicon, tellurium and selenium when it comes in contact with them, and scrupurous care should be taken in handling these elements. The reports of Moissan and others, however, are too brief to make the matter clear. The present authors know cases in which the reaction made no remarkable progress during their experiments with fluorine, though they felt at first uneasy about the danger of burning. The authors examined the conditions for the combustion of these inflammable solids so that they might thence be able to handle fluorine with confidence. The results of qualitative experiments on the reactions between fluorine and charcoal, phosphorus, sulphur, or selenium are given below:

(1) *Reaction between stationary gaseous fluorine and solids.* A spring balance similar to one used in the study of adsorption of fluorine gas was adopted in this experiment. About 1 g. of each sample was placed on a scale attached to the lower end of the balance and fluorine was slowly introduced. Then the change in the sample and spring was observed. The results of the experiment at 0°, 15° and 30°C. were as follows: (i) Red phosphorus showed reaction at these temperatures, and its quantity decreased. At 15°C., it emitted white smoke at the moment when the fluorine gas was introduced, while at 30°C. it burst into blue flame. (ii) Sulphur emitted white smoke at 15°C. and 30°C., but without flame. (iii) Selenium gave the same phenomenon as seen with sulphur. (iv) Charcoal emitted neither smoke nor flame at any of these temperatures, and was the most inactive.

(2) *Experiment in flowing gas.* As stated above, some substances do not burn in stationary fluorine at ordinary temperature. But even these substances burnt at the moment when, or a little after, they were exposed to fluorine jetting out of a small bore of a tube. It seems that the combustion takes place in a certain range of velocity of the gas flow. Of course this depends upon the bore of the pipe and, therefore, cannot be said to be an established fact. The experiment was carried out by means of an apparatus illustrated in Fig. 4.

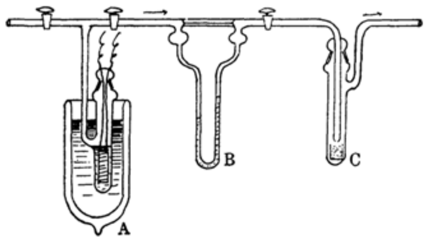

Fig. 4.

Although charcoal did not burn in stationary fluorine gas at ordinary temperature, it did at 15°C. on coming in contact with a flow of fluorine running at a velocity of about 60 c.c./min. The combustion of the samples as related to the velocity of the fluorine gas flow was as follows:

Sample	Phosphorus	Selenium	Sulphur	Charcoal
Velocity of flow (c.c./min.)	15	20	22	60

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