

# THE ELECTROLYTIC PRODUCTION OF FLUORINE<sup>1</sup>

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Fluorine was first prepared in quantity by H. Moissan<sup>2</sup> by the electrolysis of anhydrous hydrofluoric acid rendered conducting by the addition of potassium hydrogen fluoride. Moissan began with a platinum U-tube as his electrolyzing

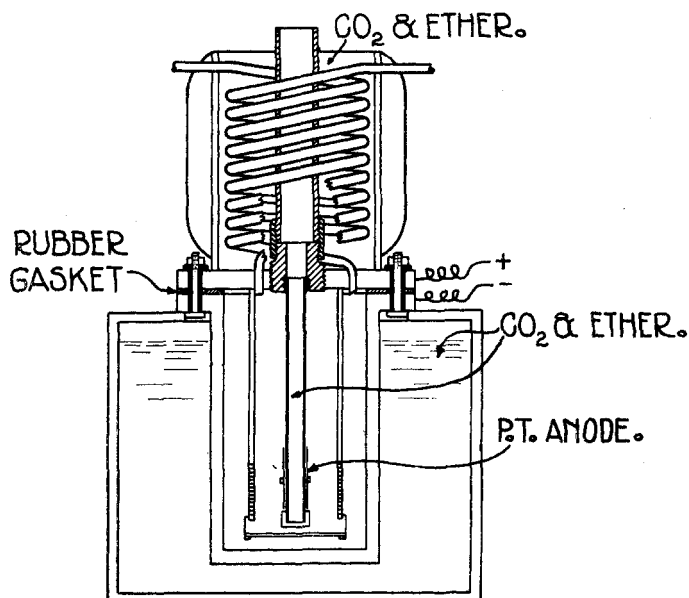


Fig. 1

vessel, the openings in which were closed with fluorite stoppers in which the electrodes of platinum-iridium were set. Later he found that copper would serve equally well as an electrolyzing vessel but that platinum electrodes must be used, Fig. 1. With copper electrodes, polarization took place due

<sup>1</sup> Published by permission of the Director of the Chemical Warfare Service.

<sup>2</sup> Comptes rendus., 102, 1543 (1886); 103, 202, 256, 850 (1886); 109, 362, 637 (1889).

to the formation of a non-conducting film of copper fluoride on the anode. Owing to the heat generated in the electrolysis and the high vapor pressure of hydrofluoric acid under usual laboratory conditions, it was necessary to keep the cell well cooled. In his earlier experiments, Moissan effected the cooling by the evaporation of chlormethane. Later he used acetone containing solid carbon dioxide. Other investigators have used calcium chloride freezing mixture<sup>1</sup> and alcohol and solid carbon dioxide.<sup>2</sup>

The usual method of preparing anhydrous hydrofluoric acid was to heat potassium hydrogen fluoride.<sup>3</sup> Moissan decomposed the anhydrous salt in a platinum retort. Ruff and Plato,<sup>4</sup> and Goldschmidt<sup>5</sup> replaced the platinum retort by a copper one and found that this latter was not acted on appreciably. Ray and Banta confirmed this result.

Two explosions occurred at this laboratory while distilling the hydrofluoric acid from the double salt. The cause of the explosions was in both cases a clogging of the copper tubing leading to the condenser by particles of potassium fluoride carried along by the gaseous hydrofluoric acid. To avoid this, a copper retort was fitted with a distilling column an inch in diameter which was closed with a brass cap that served as a safety valve. Two tubes entered the distilling column near the top; one leading to the copper condenser, the other serving to admit air through a sulphuric acid wash-bottle. The condenser was joined by copper connections to a receiver also protected by a wash-bottle of sulphuric acid.

A very slow stream of air was caused to pass through the apparatus during the distillation. The absence of bubbles indicated that the pipe line was obstructed. The receiver and the condenser were cooled by an ice-salt mixture.

Experiments were made with the Moissan and with the Meslans type of cell, using platinum anodes. While some

<sup>1</sup> Ruff and Ipsen: *Ber. deutsch. chem. Ges.*, **36**, 1777 (1903).

<sup>2</sup> Cuthertson and Prideaux: *Phil. Trans.*, **205**, 319 (1905).

<sup>3</sup> Fremy: *Ann. Chim. Phys.*, (3) **47**, 6 (1836).

<sup>4</sup> *Ber. deutsch. chem. Ges.*, **37**, 673 (1904).

<sup>5</sup> *Monatsheft*, **28**, 297 (1897).

fluorine was obtained, the platinum anodes were attacked even though the temperature of the cell was kept at  $-30^{\circ}$  to  $-60^{\circ}$ . It was quite evident that the corrosion of the platinum anode was so great that fluorine could not be made commercially in this way. An Acheson graphite anode containing 98 percent graphite was tried; but it swelled and disintegrated even when no current was passing. The action appeared to be due to the hydrofluoric acid rather than to fluorine.

Since potassium hydrogen fluoride melts at approximately  $200^{\circ}$  and decomposes but slightly at this temperature, it was determined to try to obtain fluorine by electrolyzing the fused salt. It was found that a graphite anode could be used. The final form of the cell is shown in Fig. 2. The

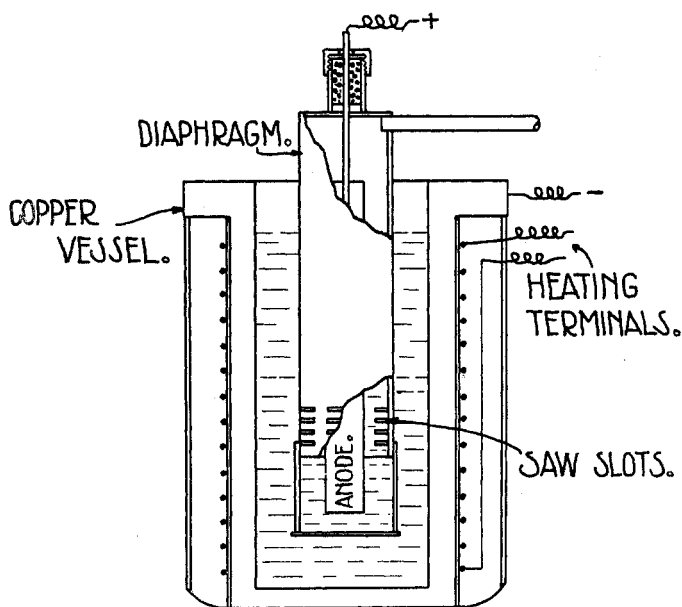


Fig. 2

electrolyzing vessel which served as cathode was of heavy copper,  $3\frac{1}{2}$  inches internal diameter and 8 inches deep, surmounted by a heavy flange. The cell was wound with nichrome wire insulated from the wall with asbestos paper.

To prevent loss of heat by radiation the wires were surrounded by asbestos wool and asbestos paper. The diaphragm was two inches in diameter. Near the bottom a number of slots were cut for the purpose of decreasing the voltage of the cell. Hydrogen evolved from the bottom of the electrolyzing vessel during electrolysis was prevented from rising to the inside of the diaphragm where it would unite with fluorine, by means of a false bottom which deflected the bubbles. Considerable space remained below the anode for potassium fluoride to collect. The graphite anode was insulated by packing it in a mass of finely powdered fluorspar, held closely and firmly round a copper bolt by means of a packing gland and nut. The copper lead was held in place by a washer of fluorspar while the finely powdered mineral was pounded in. Finally, a fiber washer was placed on top and the packing nut screwed down securely. The graphite anode was attached to the copper terminal by boring a hole in the former and pounding it firmly onto the latter.

The fused bath has a slight solvent action on copper vessels so that there is a gradual accumulation of copper fluoride in the bath. The solvent action increases with rising temperature and when there is a localized overheating such as is obtained with a Bunsen burner, it takes but a short time for a hole to be eaten through the vessel at the point it is heated. The local disintegration of the vessels has been overcome in large measure by electrical heating. In an electrically heated cell containing approximately 1500 grams of bath about 20 grams of  $\text{Cu}_2\text{F}_2$  were formed in a week.

A fresh bath, prepared from potassium fluoride and commercial hydrofluoric acid, always contained some water which had to be electrolyzed out at a low current density before fluorine was obtained. If the current density was too high, polarization resulted and the voltage rose to 50 or 60 volts. There was sparking through the oxygen gas film that suffused the bath with a blue luminescence. A current density of 2 to 3 amperes per square decimeter was passed until a test of the anode gas showed the presence of fluorine, after which

a much higher current was used without polarization resulting.

A difficulty which proved very troublesome indeed for a time was the foaming of the bath, particularly around the anode. This frothing carried up the electrolyte into the exit tube of the diaphragm where it froze and clogged up the system. Frothing resulted only after the bath had been electrolyzed for a considerable length of time so that the electrolyte had become viscous with the accumulation of potassium fluoride and copper fluoride. To prevent it, all that was necessary was to add hydrofluoric acid and regenerate the bath. Before it was found that regeneration would solve the difficulty, stirring the bath and shaking the anode by a motor were tried without avail. Simply grinding up the salt and adding hydrofluoric acid without filtering the solution to remove impurities serves to put the bath in good shape so far as frothing goes.

Since the electrolytic decomposition of potassium hydrogen fluoride results in a loss of hydrofluoric acid and the consequent formation of potassium fluoride it is necessary to regenerate the bath from time to time. Inasmuch as the potassium fluoride is not molten at the temperature of the bath it gradually settles to the bottom of the electrolyzing vessel. Attempts have been made to run anhydrous hydrofluoric acid into the bath under pressure but these have not proven successful since the acid is a gas and it merely bubbles through the molten double salt and reacts but slowly if at all with the solid on the bottom of the cell. Furthermore, in view of the fact that the bath dissolves copper slightly it is necessary occasionally to dissolve the electrolyte in water and filter off the impurities. During this operation the hydrofluoric acid can be added to the cell.

The procedure followed in this laboratory has been as follows: After using the bath until it becomes quite viscous as a result of the presence of considerable solid KF it is poured into a copper dish or on a sheet of copper. After cooling, the salt is crushed fine, placed in a copper vessel, and commercial

hydrofluoric acid added. As a rule, the salt is considered as all KF and enough acid is added to form  $\text{KHF}_2$ . Inasmuch as there is always considerable  $\text{KHF}_2$  present in the bath when poured out, a reasonable excess of acid is ensured. The bath with its excess of acid is heated slowly for several hours and finally brought to  $225^\circ$  when it is easily molten. It is then returned to the cell and a current of 2 to 3 amperes per square decimeter is passed for several hours to electrolyze out the water. It has been noticed that as the last traces of water are removed a temperature of from  $240^\circ$  to  $250^\circ$  is necessary to keep a molten electrolyte.

In order to prevent contamination of the bath by copper and the consequent necessity for dissolving up and filtering off the bath, a Dixon graphite crucible was substituted for the copper electrolyzing vessel. It was rapidly attacked, however, owing to the high percentage of clay in its make-up. A vessel made from graphite boards was next tried but the structure was such that it absorbed a large amount of hydrofluoric acid and so proved unsatisfactory. It is proposed to try a crucible of electrode graphite such as is used for the anode as soon as one can be secured. If this proves satisfactory the regeneration may be effected in the cell, without much difficulty. If anhydrous acid is used instead of the commercial product the period of drying and preliminary electrolysis to remove water will be materially shortened.

In the first cells used the voltage was 18 to 20 volts for a current of 3 amperes. This seemed higher than necessary. Accordingly the vessel was used as the cathode thereby decreasing the current density of this electrode; and the anode was dropped an inch below the diaphragm. With this arrangement it was found possible to pass 10 amperes at 12 volts. At a temperature of  $240^\circ$  to  $250^\circ$  a voltage of 15 was usual with a current of 10 amperes. At higher temperature the conductivity of the bath increased appreciably but loss of hydrofluoric acid offset this advantage. Working with ten amperes at 12 to 15 volts and a temperature of  $225^\circ$ – $250^\circ$ , the current efficiency is about 70 percent.

Among the tests for fluorine may be mentioned the following:

1. The not unpleasant odor of small quantities of fluorine is very characteristic. The odor reminds one somewhat of a mixture of ozone and chlorine but without the irritating action of the latter. This test readily serves for detecting leaks in the apparatus. Apparently fluorine possesses but little toxic action although long exposure to rather large quantities produces headache.

2. The unlighted gas mixture from a Bunsen burner is instantly ignited by fluorine. This test is delicate but less so than the odor.

3. Sulphur is ignited quickly by the gas. A soft charcoal, *e. g.*, a piece of charred wood glows brilliantly. Selenium reacts with fusion. Chloroform vapors react readily.

On account of the difficulties involved in the preparation of thoroughly dry potassium acid fluoride it occurred to us that the anhydrous acid could be prepared with considerably less difficulty if sodium acid fluoride were substituted for the potassium salt usually employed.

The following are among the more noteworthy advantages:

1. Sodium fluoride is not hygroscopic and hence over-drying of the double salt does not leave a material that has to be protected from the air; potassium fluoride on the other hand is very hygroscopic indeed.

2. The sodium salt decomposes below the fusion temperature while the potassium salt does not.

3. The sodium salt is cheaper.

4. The sodium salt contains a higher percentage of available hydrofluoric acid.

Two grams of sodium fluoride were treated with an excess of aqueous hydrofluoric acid. The reaction took place rapidly with the evolution of heat. The excess hydrofluoric acid was driven off, the product was dried at  $260^{\circ}$  for a few minutes and weighed. The gain in weight corresponded to 23.6 percent hydrofluoric acid. On heating again for a few minutes to  $260^{\circ}$ , a further loss of hydrofluoric acid to 20.9

percent was found. It was evident that  $260^{\circ}$  was too high a temperature for drying so the experiments were repeated at a temperature of  $140^{\circ}$  to  $160^{\circ}$ . The percentage hydrofluoric acid taken up was 32.3 which is theory. This percentage was reduced to 32.14 by drying a second time, at  $140^{\circ}$  to  $160^{\circ}$ .

With the present apparatus it is possible to show the properties of fluorine as a regular lecture experiment involving no especial difficulties. If one were to make fluorine on a commercial scale, it is quite probable that it would be desirable not to make the containing vessel the cathode and it is also probable that external heating would cease to be necessary.

This work was done in the Catalytic Laboratory of the Research Division of the Chemical Warfare Service under the general supervision of W. D. Bancroft.