[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

A Fluorine Generator

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Laboratory fluorine generators have been described and discussed in this Journal.[1-5] Good as they are, they are not fitted for rough, continuous usage, and they are expensive to construct. The generator described here is derived from that of Dennis; it can be built rapidly and cheaply, as it is made of standard materials, and is assembled by simple welding. It has been operated continuously for weeks with a minimum of attention. Corrosion did not destroy it before several months of exceedingly rough treatment.

Cell.—The generator cell is made of two pieces of copper tubing welded in the shape of a V, as recommended by Dennis. The dimensions indicated, *i. e.*, 30 cm. in length, 5 cm. in diameter, and the 70° angle are retained, because they are convenient for a laboratory apparatus. However, standard copper tubing is used instead of so-called "double duty," and the thermometer well in the welded angle of the V is eliminated. Besides savings in cost and weight, the main object of these modifications is to make the task of welding so simple that it can be performed in any automobile body repair establishment at very low cost and in a few minutes.

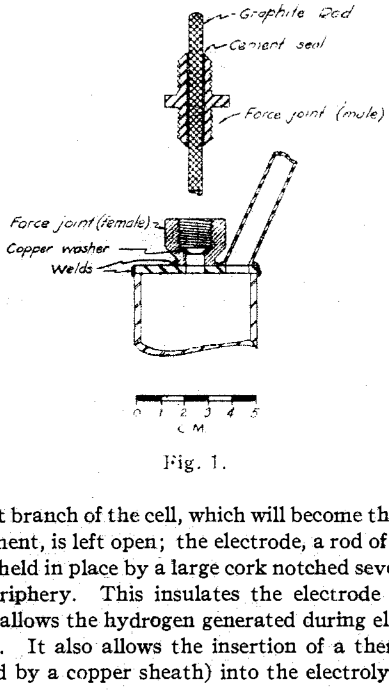

Fig. 1.

The left branch of the cell, which will become the cathode compartment, is left open; the electrode, a rod of graphite, is simply held in place by a large cork notched several times on its periphery. This insulates the electrode from the shell and allows the hydrogen generated during electrolysis to escape. It also allows the insertion of a thermometer (protected by a copper sheath) into the electrolyte. This protecting sheath is made of a piece of copper tubing, the end of which is crushed shut by a hammer blow.

The right branch, which forms the anode compartment where fluorine will be liberated, is welded shut by means of a copper disk. This disk is then pierced by two holes, one in the center to give passage to the anode, and one close to the periphery where the copper delivery tube will be welded. The female half of a force joint is fitted at the center hole and welded in place. To complete the cell, a heating wire or ribbon is wound around both branches, which are then covered by a light insulating coat. Steam pipe covering held by asbestos tape is adequate.

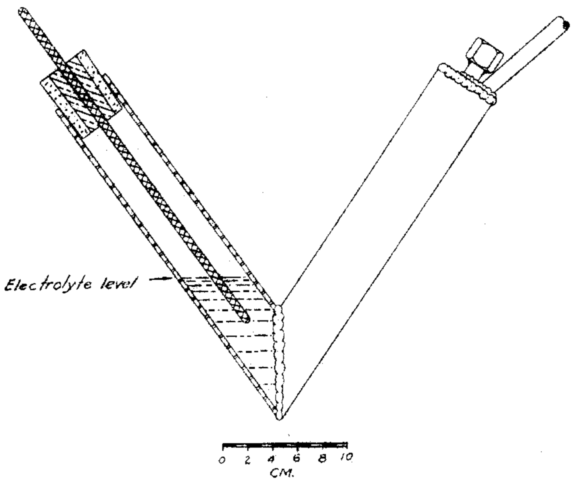

Fig. 2.

The anode is mounted, by means of Portland cement, or some polymerized varnish, in the male half of the force joint. A copper washer is inserted in the joint, when the anode is put in place. Tightening squeezes this washer and makes the joint assembly impervious to fluorine, thus protecting the threads. The copper washer is the only part which requires occasional replacement. Standard copper tubing and force joints of any dimension are obtainable from heating supply firms and from refrigerator dealers. No mechanical work is required but a little sawing and drilling, and the welding is very simple.

Electrolyte and Electrodes.—The electrolyte should be a good grade of commercial potassium acid fluoride but there is no need to use a specially manufactured salt; and graphite electrodes of spectrographic grade are sufficient. The acid fluoride of commercial grade contains water and silicates, and so also do the electrodes. The adverse influence of these substances is well known. However, purification can be accomplished conveniently by electrolysis. As long as water is present, hydrogen and oxygen will be generated, but when this water is almost completely removed, it will be observed that a glassy silicate coating builds up on the electrodes and this interrupts the electrolysis. The electrodes are then removed and replaced by fresh

(1) Simons, THIS JOURNAL, **46**, 2175 (1924).
(2) Schumb and Gamble, *ibid.*, **52**, 4302 (1930).
(3) Dennis, Veeder and Rochow, *ibid.*, **53**, 3263 (1931).
(4) Dennis and Rochow, *ibid.*, **56**, 879 (1934).
(5) Miller and Bigelow, *ibid.*, **58**, 1585 (1936).

ones, a very easy task if spare anodes mounted on force joints have been prepared. Sandpapering removes the glassy silicate from the electrodes, which are then ready to be reinserted in the generator when a glassy coat has again covered the ones in place. This silicate coating occurs mostly at the anode, and therefore the anodes must be replaced more often than the cathodes. After a few substitutions, the coating no longer forms and the generation of fluorine proceeds smoothly.

In order to electrolyze KF·HF, one has to operate in a temperature range of 260 to 300° which causes rapid corrosion of the fluorine cell. However, since good anhydrous hydrofluoric acid recently has been made available commercially in steel containers of convenient size, it has become more practical to electrolyze a salt whose composition is approximately represented by KF·3HF. The low melting point of such a salt makes it possible to carry out the electrolysis at from 70 to 100°, thereby minimizing corrosion and lengthening the equipment's life.[6]

After the electrolyte has been freed from water and silicates and when the generation of fluorine has become smooth, the operation is interrupted. Before cooling occurs a steel container of hydrofluoric acid is connected by means of flexible copper tubing and force joints, to the fluorine delivery tube of the generator, the valve on the acid tank is opened and the apparatus allowed to stand undisturbed overnight. Dry hydrofluoric acid vapors are sucked into the anode compartment and absorbed by the electrolyte with a gentle heat evolution which is sufficient to maintain the mass liquid, thereby automatically making KF·3HF.

Electrolysis.—Except for the temperature, the electrolysis is conducted as recommended by Dennis, and it gives the yields indicated by him in relation to the power used; it develops almost enough heat to maintain the electrolyte in the 70 to 100° range. At the end of the day's work, the cell is connected to the hydrofluoric acid tank and allowed to replenish the spent acid overnight. If no acid is needed, the generator is merely kept warm overnight. This mode of operation lengthens the life of the cell but does not make it eternal. Corrosion of the copper cell takes place, finely divided copper spreads in the electrolyte, and the electrolysis is progressively impeded. This copper can be removed, but for laboratory use it is held more convenient to discard the damaged salt, and replace it by a fresh batch, which is rapidly purified as indicated above.

Optional Modifications.—In the course of several experimental runs, it was found that the anode did not have to be insulated from the copper shell, when the production of fluorine was well under way. Fluorine was generated exclusively on the carbon and not at all on the copper. However, it was found impossible to operate in this fashion as long as water and silica were present. No explanation is offered for this behavior, and it was decided, as a matter of expediency, to continue mounting the anodes in the force joints by means of an insulating binder.

A second modification was then tried. Instead of using long rods of graphite, short graphite stubs were screwed in place at the end of a copper rod, and the copper rod was mounted without insulation in the force joint. This did not affect the fluorine generation, but proved somewhat fragile and the graphite occasionally broke at the threaded part. Long graphite rods do break sometimes, but very infrequently. The only redeeming factor of the short electrode was the fact that when it broke off, it was easy to push the carbon stub over into the cathode compartment, where it would bob up and could be removed with a pair of tweezers. To effect this, the anode was removed and a tool made of twisted baling wires was rammed through the opening. It thus appears that either type of electrode will do.

The task of simplifying and operating the generator cell until a robust practical outfit was obtained has been done with the help of D. F. Helm, J. R. Long and R. A. Ewing, to whom most of the credit should go.

Summary

A simply and inexpensively constructed fluorine generator is described. Made of copper, it is a rugged apparatus in which KF·3HF can be electrolyzed continuously for long periods of time.

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(6) The use of a salt containing several molecules of hydrogen fluorides has been proposed previously, but was not made practical [see Lebeau, *Bull. soc. encour. ind. nat.*, **139**, 15–35 (1927)]. For a good discussion of the KF·HF system, see Cady, THIS JOURNAL, **56**, 1431 (1934).