lected on a filter and washed with cold absolute alcohol and with ether; yield, 4.1 g., or about 13.5%.

If the products of reaction are allowed to stand for some time before the hyponitrite is separated, sodium nitrite may form and contaminate the salt.

Silver Hyponitrite.—The calculated amount of a 5% solution of silver nitrate in water was added to a cold, dilute aqueous solution containing 4 g. of sodium salt. Silver hyponitrite was precipitated at once; it was collected, washed with water, then with absolute alcohol and with ether. Dried in a desiccator, it weighed 10.3 g. A sample was analyzed by the Volhard method.

Anal. Subs., 0.2899: cc. of 0.1208 *N* KSCN, 17.36. Calc. for $Ag_2O_2N_2$: Ag, 78.24. Found: 78.04.

Summary

1. Various methods of preparing hyponitrites have been described.

2. The preparation of sodium hyponitrite from hydroxylamine, sodium ethylate and ethyl nitrite is described.

3. Sodium hyponitrite is quite stable and is a source from which silver hyponitrite may be prepared easily.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE PREPARATION OF FLUORINE

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An unusual interest attaches to the chemistry of fluorine and its compounds on account of the extremely electro negative character of the element. Comparatively little attention has been paid to this field, however, due to the experimental difficulties involved, so that further investigations are very important. A necessary preliminary to such work is the development of the technique for the preparation of elementary fluorine in large quantities.

The electrolysis of anhydrous hydrofluoric acid, used by Moissan[1] in the first isolation of the element, is difficult and expensive, and like the decomposition of lead tetrafluoride described by Argo, Mathers, Humiston and Anderson[2] is not promising as a method of preparing large quantities of fluorine. The most satisfactory method for this purpose is the electrolysis of fused potassium acid fluoride as described by the authors just mentioned. Their cell consists of an electrically heated copper vessel which serves both as cathode and as a container for the electrolyte. In

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[1] Moissan, *Compt. rend.*, **102,** 1543 (1886); **103,** 202, 256 (1886).

[2] Argo, Mathers, Humiston and Anderson, *Trans. Am. Electrochem. Soc.*, **23,** 348 (1919).

this is suspended a copper bell or diaphragm containing an insulated graphite anode.[3]

This generator gave fluorine when first set up but was not dependable after having been run for some time. Three difficulties were encountered in its use: first, foam arising from the bath congealed in the delivery tube and finally obstructed it; second, the method of regenerating the electrolyte was laborious, consisting of dissolving the spent salt in water, filtering to remove copper fluoride and other impurities, adding aqueous hydrofluoric acid, evaporating the water, and then electrolyzing out the last traces of water with the salt in the generator; third, after the generator had been run for some time, the anode became short-circuited to the diaphragm through the insulating seal.

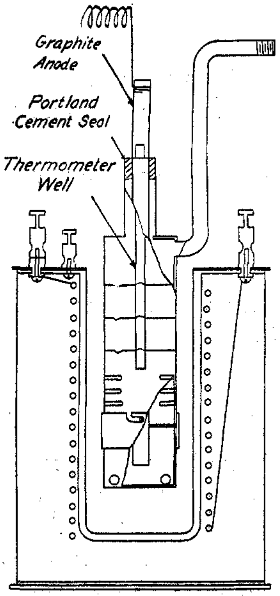

Fig. 1.—Fluorine generator.

It was important in our work to be able to generate fluorine in whatever quantities desired over long periods of time and without too much attention to the generator, as the experiments themselves required considerable manipulation. It was therefore necessary to develop further the technique of this method of preparation.

The first difficulty was easily overcome by using a vertical delivery tube of large size, shown in Fig. 1. It was heated occasionally during the electrolysis to melt the accumulated salt and permit it to run back into the generator. We tried to heat this vertical portion of the delivery tube electrically so that the salt would flow back continuously but found this of no value, as the salt then solidified further on in the tube.

The overcoming of the second difficulty followed improved technique in the regenerating of the bath. At first it was thought necessary to remove the accumulated copper fluoride every time, but as the fused salt dissolves slowly in water and forms a large quantity of aqueous solution, which requires filtration and evaporation, we tried to avoid this operation. Filtering the molten salt through copper gauze was found to be effective in removing some solid impurities. The following procedure was finally adopted to regenerate the electrolyte. The exhausted salt was dipped

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[3] Meyer and Sandow [*Ber.*, **54**, 759 (1921)] later developed an apparatus for carrying out this same reaction, but it is more complicated, breaks if the salt is allowed to cool in it and seems obviously inferior to the apparatus of the American investigators. It is evident, also, that their generator would be subject to the same difficulties as are described in this paper.

with a copper ladle from the generator to a tall copper vessel and allowed to solidify. An excess of aqueous hydrofluoric acid was then added and the mass heated until it was all molten. A copper diaphragm provided with a graphite electrode, similar to the one used in the generator, and a copper-incased thermometer were then put in place. The copper diaphragm was made from a piece of 6-cm. thin-walled copper tubing. Saw slots were cut in it to give free passage to the solution and the bottom was closed to prevent access of hydrogen to the fluorine later evolved from the anode. This made a sort of crude electrolyzing cell with no means of collecting the gas evolved. An electrolyzing current was passed, the temperature of the bath brought slowly to 200–220°, and electrolysis carried out at that temperature until all the water was removed. This point was marked by the liberation of fluorine at the anode. The liquid was then decanted from the solid copper fluoride and other impurities at the bottom of the vessel. It was allowed to solidify in a flat, copper dish and when cold was broken into pieces of convenient size. The fused, anhydrous acid salt does not take up water from the air and so remains in a condition to be placed in the generator and used at any time. With a supply of this material on hand it was possible to stop the generator, remove its exhausted charge, recharge it and deliver fluorine from it again in less than two hours. The potassium salt was recovered from the accumulated residues by leaching with water. As the greatest amount of corrosion of the anode occurred at the time the last traces of water were being removed, this method saved the anode of the generator. It was found advantageous to start the electrolyzing current before the aqueous salt was heated to 100°, as this helped to prevent boiling over. When most of the water had been removed the cell had a tendency to polarize with arcing around the anode. This persisted until all the water had been removed. A greater current can be used with safety when the electrolysis is carried on in an open vessel, and so the time of dehydration is greatly reduced. A new charge was always in preparation while the generator was in operation.

The original acid salt was made from commercial 50% acid and potassium hydroxide. The acid was placed in a tall copper pot, a copper screen was placed over it, and the sticks of the hydroxide were placed on the screen. The fumes from the acid slowly melted the sticks and the liquid ran down and neutralized the acid. In this manner danger from the violence of the reaction was avoided and at the same time a large amount of water was not introduced.

With the generator in operation, a potential of 10 volts across the electrodes gave a current of 10 to 15 amperes, evolving fluorine at the rate of about 4 liters per hour. It was found possible to run the generator continuously at this rate for 20 to 30 hours. The temperature at the start was about 220°. It was necessary to increase this as the electrolysis progressed to 280° or 300° in order to keep the bath molten at the end of the run.

In order to save time the experiments were usually planned to permit use of all the fluorine given from one charge of the generator at one time. In this way the time necessary to melt the salt and to remove, by electrolysis, the water which the bath had absorbed from the air, was eliminated. Normal potassium fluoride, unlike the acid salt, is very deliquescent, and the partially depleted electrolyte contains this material; and so although the freshly prepared salt remains dry indefinitely in the laboratory air, it becomes more and more deliquescent as it is used. When the amount of fluorine generated from it is small, it can be used intermittently for weeks before it will absorb sufficient water to give trouble.

The third difficulty encountered in the apparatus constructed according to Argo, Mathers, Humiston and Anderson, namely, the short-circuiting of the anode to the diaphragm, made it necessary to remove and reseal the anode frequently. It was found that the copper rod which held the electrode was corroded and the copper was apparently distributed over the seal, making it a conductor. Various materials were tried, such as powdered fluorite as recommended by Argo and his associates, and cryolite poured while molten. All such materials acted in a similar manner. The graphite anode was then led through the diaphragm and the copper rod eliminated. Various materials were tried for sealing in the anode but Portland cement was found to be the best. It was very easy to use, as no stuffing gland or similar device was necessary. After the fluorine gas had acted on it for only a short time it became a hard impervious seal. A copper connection was soldered to the top of the graphite rod.

The generator that we used is illustrated in Fig. 1.

It was made entirely of heavy copper tubing and plate, the parts being melted together where necessary, as at the bottom of the containing vessel, otherwise force fits being used. The copper well for the thermometer (which was coated with a heavy chlorinated oil) was held to the side of the diaphragm by means of copper wire. The lower portion of the diaphragm, whose function was to keep the hydrogen bubbles from the bottom of the vessel from entering the fluorine chamber, was fastened to the upper portion with a bayonet joint. Fairly large holes were drilled in this to permit the solid potassium fluoride to find its way out of the central portion to the bottom of the vessel. The heating element consisted of No. 16 Nichrome wire which had a total resistance of 12 ohms. With the method of regenerating the salt described, which kept it saturated with copper fluoride, very little corrosion of the copper parts occurred.

The current efficiency of this method of preparation has been shown by Argo and his associates and also by Meyer and Sandow to be about 70%. The only impurities that the gas could contain after the water had been completely removed from the electrolyte are hydrogen fluoride from the bath and carbon fluorides from the reaction of the fluorine with the graphite electrode. The former is easily and completely removed by passing the gas through dry sodium fluoride, while the latter, according to Meyer and Sandow, are present in extremely small amounts.

Summary

The fluorine generator described by Argo, Mathers, Humiston and Anderson has been improved. The technique for the regeneration of the electrolyte and for the continuous generation of large quantities of fluorine has been developed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE PREPARATION, FREEZING POINT AND VAPOR PRESSURE OF HYDROGEN FLUORIDE

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The Preparation of Anhydrous Hydrofluoric Acid

Frémy[1] was the first to make anhydrous hydrofluoric acid, distilling it from potassium acid fluoride. Later Gore[2] prepared the material in the same manner and studied many of its properties. We have found that heating the acid fluoride to fusion, as done by Gore and others[3] does not suffice to dehydrate it completely. Argo, Mathers, Humiston and Anderson[4] recommend the use of the sodium salt in place of the potassium salt and enumerate certain advantages, but it is quite evident that the complete dehydration of the sodium salt would involve the same difficulty.

In the preceding paper a method is given for the preparation of the anhydrous potassium salt by electrolyzing out the last traces of water. This gave a material from which anhydrous hydrofluoric acid could be prepared, and the next step was to develop an apparatus for the distillation. Argo and his associates encountered difficulties in this process due to the obstruction of the exit tube by the solidification of foam therein. We have been able to construct an apparatus (Fig. 1) which avoids this difficulty as follows.

A heavy copper retort is heated by a large blast ring burner so as to apply the heat near the surface of the molten charge. The lid is clamped on with "C" clamps, and the joint made tight by means of a copper washer with annular corrugations. The exit tube leading from the lid is 1 meter long and 2.5 cm. in diameter. It has a chamber

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[1] Frémy, *Ann. chim. phys.*, [3] **47**, 6 (1836).

[2] Gore, *J. Chem. Soc.*, **22**, 368 (1869).

[3] Thorpe and Hambly, *ibid.*, **55**, 163 (1889). Ruff and Plato, *Ber.*, **37**, 673 (1904).

[4] Argo, Mathers, Humiston and Anderson, *Trans. Am. Electrochem. Soc.*, **35**, 335 (1919).