

THE CONSTRUCTION AND USE OF A FLUORINE GENERATOR

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OBJECT

The object of this research has been to construct and operate a fluorine generator with the aim of improving upon present practice. The work has been divided into three sections. First, to construct a generator according to the most satisfactory methods reported in the literature. Second, to modify the construction of the most promising of these generators where changes appear advisable. Third, to investigate the possibility of producing fluorine by the electrolysis of materials other than solutions of alkali fluorides in anhydrous hydrogen fluoride commonly employed for this purpose.

PREVIOUS WORK

The first successful attempt to isolate fluorine was carried out by Henri Moissan¹ some time in the year 1886. This was the result of a number of attempts to prepare fluorine carried out over a period of three years. Moissan's first experiments were attempts to prepare the element by the decomposition of gaseous fluorides, but when even the use of a platinum plate at red heat failed, it was evident that other methods than the decomposition of available fluorides would have to be used. Moissan next tried to prepare fluorine by the electrolysis of pure liquid hydrogen fluoride. However, this material was found to be a non-conductor of electricity in the pure state. The addition of a small amount of potassium fluoride, however, gave a solution which conducted. This method of electrolysis results in the production of fluorine, but the formation of oxygen and ozone at the anode is the result if the slightest trace of water is present.

The apparatus employed by Moissan consisted of a platinum-iridium U-tube with a platinum anode. Investigation of the anode at the end of the run

showed that considerable attack had occurred but the container showed little wear. The open ends of the tube were fitted with flucspar stoppers ground to fit the tubes and bored with holes which gripped the electrodes. Lead washers and shellac were employed to make the joints air-tight. The U-tube was surrounded by a bath of liquid methyl chloride thus keeping the electrolyte cooled to -23°C . The fluorine as it left the U-tube passed through into a platinum spiral condenser, thus removing the gaseous hydrogen fluoride which escaped with the fluorine. From the condenser the fluorine passed through two tubes containing lumps of sodium fluoride, which removed the remaining HF as $\text{NaF}\cdot\text{HF}$. Using 100gms. of anhydrous HF and 25gms of KHF_2 with current supplied by 28 Bunsen cells, Moissan obtained between two and three liters of fluorine per hour. Later Moissan modified his apparatus using a copper U-tube in place of the platinum one, the copper protecting itself by the formation of a surface coat of copper fluoride. Solid carbon dioxide was used in place of the methyl chloride for the cooling bath.

All attempts at the production of fluorine

after Moissan's success were only modifications of the original work since for the most part the electrolytes were composed of mixtures of alkali fluorides and varying percentages of hydrogen fluoride. Ruff² reported successful use of ammonium fluoride in a U-tube generator. Therefore advancement in the field of fluorine production has been mainly concerned with modifications of the construction of the generators.

C. Poulenc and M. Meslans³ used a copper vessel for container and cathode. A perforated copper diaphragm was used to keep the gases apart. Platinum served for the anode. G. Gallo⁴ reported poor results with this apparatus.

W. L. Argo, F. C. Mathers, R. Humiston and C.O. Anderson⁵ used a copper container which also served as the cathode, copper tubing with slots in the bottom served for the diaphragm and a graphite rod was used for the anode. The use of sodium acid fluoride was also advised for the electrolyte since it is non-deliquescent.

Bancroft and Jones⁶ used a magnesium pot which served as the cathode; a magnesium diaphragm closed at the bottom with holes in the side of the lower wall kept the gases apart. Graphite was used for the anode

and Portland cement was used for electrical insulation.

Von Wartenberg⁷ reported a method based upon the electrolysis of a melt with the approximate composition corresponding to the formula $KF \cdot 3HF$. This apparatus was reported to have been very successful so that a detailed description will be given here. The container was made out of copper (Figure 1) and served as the cathode. A ledge of cement was held in a trough and so constructed that the cover of the container rested on the cement and did not come in contact with the vessel which also served as the cathode. Paraffin protected the cement from the action of hydrogen fluoride. A copper diaphragm was used and extended for some distance above the cover so that no frothing could permit the melt to reach the electrical insulation. The insulation was a block of florspar with a hole in the center to hold the anode. Nickel was used for the anode. A metal block with a hole for a thermometer was silver-soldered to the pot. The operation temperature was 70° . The stream of fluorine was passed through a condenser using dry ice for cooling whereby the hydrogen fluoride is removed. This generator is reported as being very satisfactory. It has the advantage that the melt is at all times protected from the air.

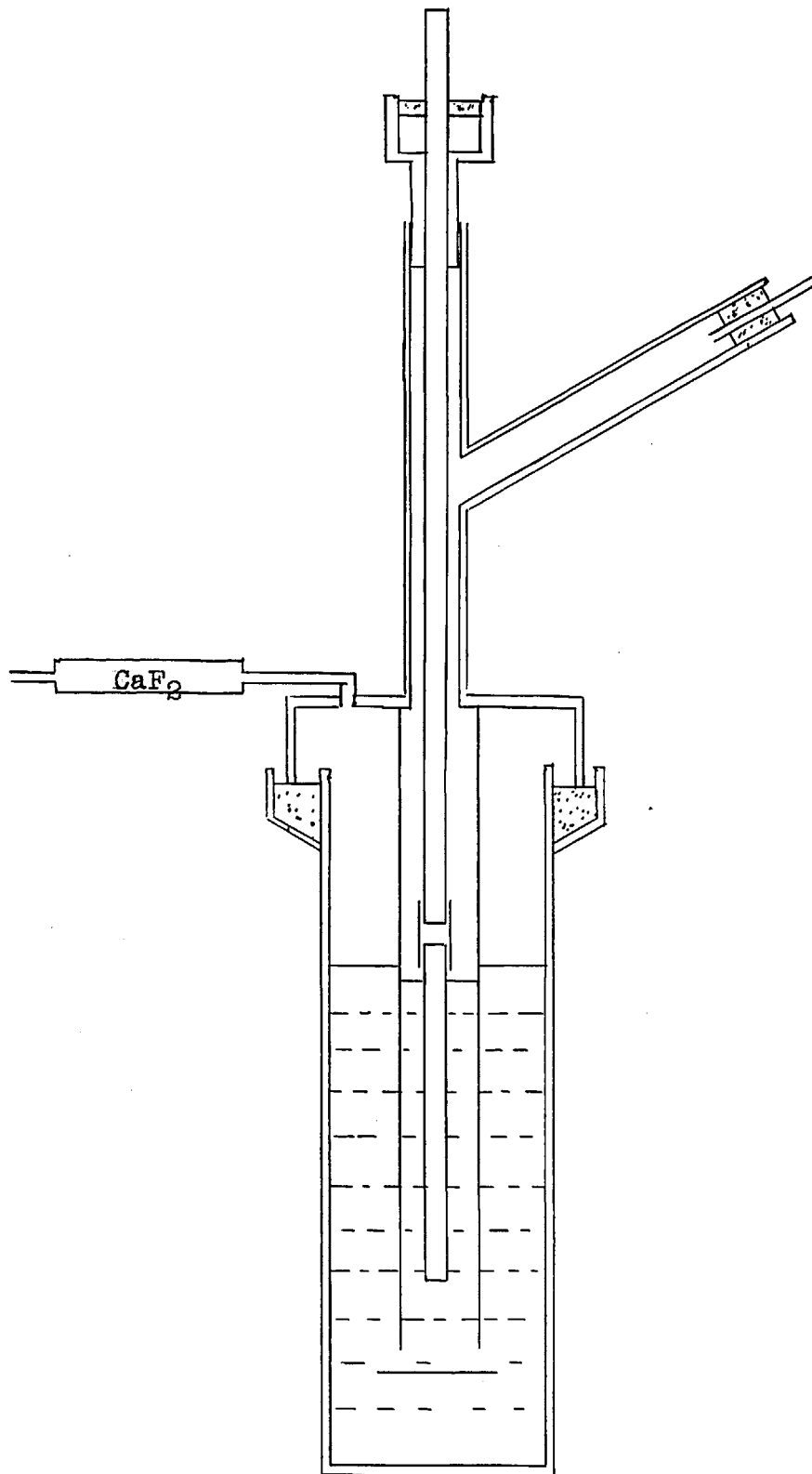


Figure 1

Gamble⁸ used a monel pot which also served as the cathode. The diaphragm was constructed of nickel. Both nickel and graphite were tried out as anodes. The graphite was found to be best at the higher temperatures used for the electrolysis of KHF_2 . Portland cement was used for electrical insulation.

Woolaver⁹ used a V-shaped pot with two monel electrodes entering through the insulation into the necks of the V.

EXPERIMENTAL

The generators that shall first be discussed were all designed for the electrolysis of a solution of potassium acid fluoride in anhydrous hydrofluoric acid. Therefore, the preparation of the melt will be described at this point with the understanding that while the composition of the melt was the same in all instances and was prepared in the same way for each electrolysis, the amount of material differed with the type of generator used.

The melt consists of a solution of potassium acid fluoride in anhydrous hydrofluoric acid with a composition approaching $\text{KF}\cdot 3\text{HF}$, or $\text{KHF}_2\cdot 2\text{HF}$. Chemically pure potassium acid fluoride (Merck) was used in all instances. Hydrogen fluoride is now available in cylinders.* The potassium acid fluoride is first placed in the electrolytic container, the tank of anhydrous hydrogen fluoride is cooled to below the boiling point (19.4°C .) and the required amount of the liquid poured from the tank into the container by tilting. Some investigators have recommended that the gas be distilled from the tank by heating and condensing in copper tubing. This was tried but was found to be a lengthy and difficult

*Purchased from the Harshaw Chemical Company, Cleveland, Ohio.

operation and quite unnecessary. The liquid hydrogen fluoride pours from the tank quite easily if there is not much hydrogen fluoride vapor. The action can be carried out at any temperature below 5° . The cooler the tank the easier the operation. The electrolyte container was placed on a platform scale and the amount of the liquid added noted and controlled by the difference in weight between the final weight and the initial weight of the container plus acid fluoride. The addition of the liquid hydrogen fluoride should best be undertaken out-of-doors. If the temperature is near or above the boiling point of the liquid hydrogen fluoride, the electrolyte container must be cooled in an ice bath until all the hydrogen fluoride has been added and has reacted with the acid fluoride. When this reaction has been completed the electrolyte will be a solid mass. If the reactants are mixed in the evening the contents of the electrolyte container should be solid and ready for heating by the following morning. The composition of the melt corresponds to the formula, $KF \cdot 3HF$, and forms a fairly stable addition compound with a melting point around 68° . The material is appreciably volatile, however, the vapor pressure of the hydrogen fluoride above the mixture increasing rapidly with increase in

temperature. The vapor pressure is sufficiently great at the melting point to necessitate the use of a condenser for the removal of the hydrogen fluoride from the stream of generated fluorine.

The condenser consists of a coil of copper tubing connected to the anode chamber at one end and to a reservoir at the other end. A straight piece of copper tube is also connected to this reservoir to carry off the fluorine after the hydrogen fluoride gas has been removed by liquefaction. The coils and the reservoir are packed with dry ice or some other suitable refrigerating material. Any suitable container can be used for the dry ice. The same condenser was used with all generators containing the solution of potassium acid fluoride in anhydrous hydrogen fluoride.

The first generator constructed (Figure 1) for the production of fluorine by the electrolysis of a solution of potassium acid fluoride in anhydrous hydrogen fluoride was a replica of the apparatus of H. Von Wartenberg (Figure 2) with a few modifications. A monel metal container that was available in the laboratory served as the electrolyte container and the cathode. It was cylindrically shaped 4.5 inches in diameter and 9 inches high fashioned from $3/32$ " monel sheet with welded seams. A diaphragm made from

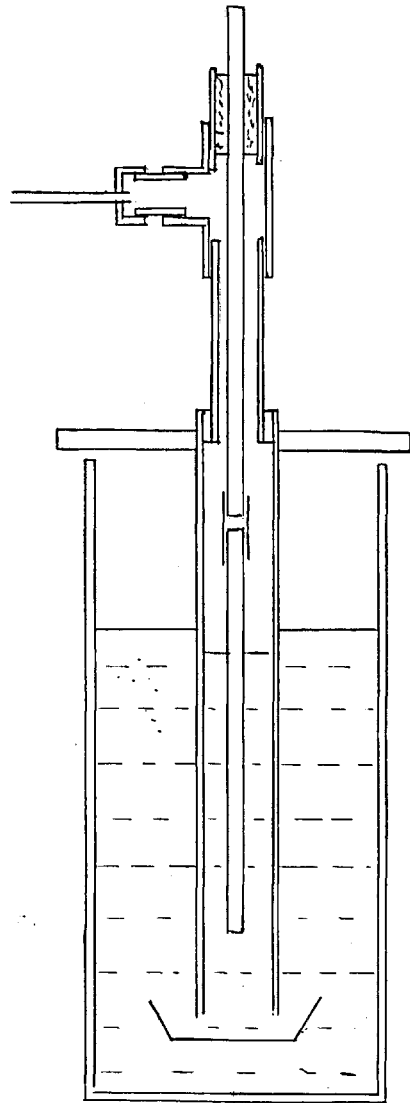


Figure 2

an eight inch piece of nickel tubing, two inches in diameter, was attached to the cover by threading so that there was a clearance of a little over an inch and a quarter between the bottom of the container and the bottom of the diaphragm. A small nickel plate is attached to the bottom of the diaphragm so that any hydrogen liberated on the bottom of the container will be prevented from rising into the anode chamber. The cover was fashioned from a brass disk 6" in diameter and $\frac{1}{4}$ " thick. A hole was made in the center and threaded to hold the diaphragm in place. Another threaded hole midway between diaphragm and container wall is equipped with a union compression such that copper tubing can be connected to carry off the hydrogen and hydrogen fluoride generated. A piece of brass $\frac{1}{2}$ " thick and of an approximate diameter of $1\frac{1}{2}$ " with a threaded 1" hole in the center, was forced into the top of the diaphragm protruding from the cover of the container. A 1" copper pipe nipple was screwed into this disk and a red brass pipe T attached to the other end of the nipple so that there was only one opening perpendicular to the axis of the nipple. A short nipple with a cap screwed to one end is

screwed into the pipe T perpendicular to the axis of the diaphragm. The cap has a threaded hole in the center for a union compression so that copper tubing can be attached to carry the fluorine to the condenser. A copper nipple is filled with Portland cement which serves to hold the anode in place through the center of the nipple and to electrically insulate it from the rest of the apparatus. This nipple is screwed into the remaining hole of the red brass T so that the anode can be inspected at will by simply unscrewing the nipple that holds it. If the anode is constructed in two parts, the lower part that extends down into the solution can be replaced at will.

The assembled generator was placed in an oil bath on a hot plate and heated until the electrolyte was completely molten. Then the hot plate was turned off and a current of five amperes was passed through the cell. The electric current alone is sufficient to maintain the bath in the molten state. Initially an aluminum anode was employed but since the cement would not adhere to the aluminum, copper was substituted and was held quite firmly by the cement insulation. After running for about fifteen minutes there was a faint explosion in the anode chamber and as the

electrolysis continued these explosions became more violent and quite frequent. The indication was that fluorine was being liberated at the anode and that some hydrogen was also finding its way into the anode chamber. It is obvious that the explosions were caused by the union of fluorine and hydrogen, since it is improbable that oxygen and hydrogen could combine at the temperature in question without some initiator such as a spark.

It was thought to be probable that the hydrogen was passing under the diaphragm. To prevent this, the plate fastened to the bottom of the diaphragm was made in the shape of a cup and the mouth of the cup, diameter 3", brought up as close as possible to the bottom of the diaphragm keeping in mind the necessity of free flow of the solution into the anode chamber. Continuation of operation of the cell, however, was followed by a considerable explosion. Investigation showed that the explosion had again taken place in the anode compartment and in this case was of such violence that the cup attached to the bottom of the diaphragm was considerably distorted.

It was thought possible that because of the

large surface area of the cathode (the interior surface of the container) the hydrogen might be forming as microbubbles and thus not rising rapidly in the solution. To eliminate this possibility an insulated nickel rod was passed through the cover of the container. Subsequent operation of the generator proved, however, that something else was basically wrong since there was little decrease in the rapidity of the explosions.

Having in mind the fact that a generator of similar construction had been reported as functioning successfully, additional work was carried out on this generator. Different types of metal were tried out as anodes, such as copper, aluminum, monel, nickel, and brass. Graphite was also tried. Of all those used the monel and the nickel stood up the best.

The electrical insulation used in the construction of this generator are the only things that differ greatly from the generator that was constructed by Von Wartenberg (Figure 1). In insulating the cover from the container a packing of asbestos paper was used with as little of the asbestos exposed to the vapors of the hydrogen fluoride as was possible. This proved to be very poor and fell to pieces very quickly. Next

a padding of rubber was used but, as with the asbestos, the rubber fell to pieces very fast. Von Wartenberg employed a cement ledge for this insulation with a coating of paraffin over the cement on the inside preventing the hydrogen fluoride from coming in contact with the cement. There was some trouble with this method as reported in the original paper, due to the creeping of the paraffin into the melt. To date, however, I believe that this is the best method for the insulating of the cover from the container. In all the containers subsequently used the cover was suspended above the container. As a result the cathode chamber was left open, and this is disadvantageous, as the electrolyte will absorb water on being exposed to the air.

Further work with this generator, resulting mostly in modifying electrical insulation of the anode from the cover, was without result. It is not apparent whether the cement insulation was at fault or whether the slight currents recorded as passing through the cement to the diaphragm were due to the formation of a film of melt across the bottom of the cement.

The author believes that any shorting is due to a formation of a coating across the bottom of the cement since the force of the explosions is sufficient to throw up part of the bath. The sides of the diaphragm showed that considerable spattering had taken place. It is, however, conceivable that the hydrogen fluoride could react with the cement to form a conducting medium. Considerable work should be done to further investigate the use of cement as an electrical insulator of the anode. There is very little action between fluorine and cement.

Since the main difficulty encountered with the above generator was the explosions, it was decided to construct a trial generator employing two diaphragms, one for the anode and one for the cathode. The generator was very simple in construction, and the same container as was used for the previous generators was used also for this one. Two pieces of $1\frac{1}{2}$ " copper pipe, 2 feet long, and threaded at one end were employed for the diaphragms. The diaphragms were suspended into the bath so that there was a space of one inch between the bottom of the container and the bottom of the diaphragms and were held in place by means of wooden

clamps. Two red brass caps were screwed on to the threaded ends of the diaphragms. A hole was drilled through the center of the caps and tapered so that spark plugs could be screwed into them. The spark plugs were attached so that the porcelain heads protruded down into the electrode chambers. The electrodes were screwed on to the spark plugs; the electrical connections were to the pins in the base of the spark plugs.

A current of five amperes was passed through this test generator, using a carbon anode and a brass cathode. The results were encouraging. There were no more explosions in the anode chamber and traces of fluorine were found to be coming from the generator by the use of starch iodide solution. After running the generator for a little over six hours the insulation of the spark plug in the anode chamber was shorted by a film of molten fluoride. It was decided to dismantle the apparatus and construct a larger scale model.

In the previous generator, which employed two diaphragms, the diameter of the container ($4\frac{1}{2}$ ") necessitated that the two diaphragms be in contact, so that the shorting of one electrode resulting in the

production of both hydrogen and fluorine in the opposite chamber. For this generator a new container was constructed (Figure 3), in a general rectangular shape, with a width of four inches and a mean length of seven inches. The container was one foot in height with welded seams, and was constructed from $1/8$ " sheet iron. Two two-foot copper pipes of 2" diameter served as the diaphragms. Spark plugs were used for insulation as before, being screwed into red brass caps which in turn were screwed on to the tops of the copper diaphragms. To prevent the action of hydrogen fluoride on the porcelain, a protecting jacket of Portland cement was cast over the porcelain. The anode was $1/4$ " carbon rod and the cathode $1/4$ " brass rod.

The generator was subjected to a current of 5 amperes, using a carbon anode and a brass cathode. There was no evidence of explosion after a run of five hours. There was no strong stream of fluorine produced, but there was some fluorine produced, as indicated by the starch iodide test. At the end of five hours the current dropped sharply and an investigation of the electrodes and the diaphragms

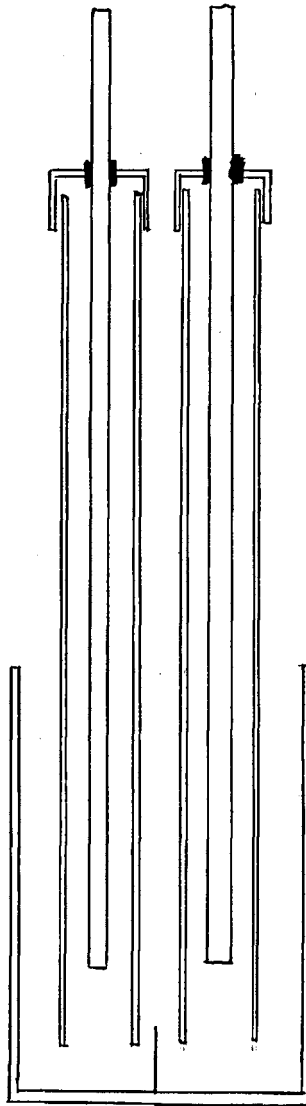


Figure 3

showed that the carbon electrode had completely disintegrated to the level of the melt. It was decided to substitute nickel for the carbon as the anode. The brass cathode was in excellent condition and showed no wear whatsoever. The interior of the anode diaphragm was completely coated with a vitreous coating of fluoride. Substitution of nickel for the carbon anode was made.

The electrolysis was again carried out for five hours at five amperes. No satisfactory stream was generated and examination of the anode showed considerable wear. Approximate temperature measurements indicated that the temperature of the bath was now considerably over the proper running temperature. This sharp rise in temperature was caused by the electrical resistance of the cell since external heating is only applied for the initial melting. Since there is no way to decrease the electrical resistance of the melt, external cooling is necessitated. At the present time, further work with this generator has been halted due to a shortage of chemicals, but will be continued as soon as more hydrogen fluoride is available to refortify the melt.

All important work on the production of fluorine has been directed towards the electrolysis of hydrogen fluoride in the presence of varying amounts of alkali fluorides. To date, work in this direction has not been particularly successful. For this reason, it was decided to investigate the possibility of electrolyzing some other compound than hydrogen fluoride. There is no information in the literature which might seem to indicate that fluorine has been or could be produced from other available chemicals. For any process to have any possibility whatsoever, it would have to possess the following characteristics. The cathode should liberate a solid or a liquid, the production of hydrogen in the classical processes being a primary disadvantage. The most important characteristic is, however, that the operating temperature must be low, preferably under one hundred degrees, and not over two hundred degrees. The reactivity of fluorine with all the known construction materials is far too great to make generation at elevated temperatures practical.

It was noted that the addition compounds of the alkali fluorides with boron trifluoride have melting

points around five hundred degrees. It was therefore thought that a eutectic mixture of alkali borofluoride might be obtained with a melting point that was low enough to make the generation of fluorine possible. Since the alkali borofluorides decompose at temperatures above 550°C ., it was decided to determine if there was a eutectic mixture of alkali fluoride with a melting point below 550° . Assuming such a mixture to exist, An attempt would be made to see if the boron trifluoride would add directly to the solution and to what extent.

Examination of the literature showed that little information was available in the way of freezing point diagrams. Since the alkali fluorides have the lowest melting points (as compared to the common alkaline earth fluorides), it was decided to confine this research to the alkali fluorides, and for economic reasons specifically to the fluorides of lithium, sodium, and potassium. There was no published material concerning the ternary freezing point system of these compounds. The freezing point diagram of the system NaF-KF was available. It was decided to construct the freezing point diagrams for the systems NaF-LiF and LiF-KF by experimental measurements. From these approximate

curves, it was hoped that a suitable composition mixture might be derived with the properties desired. It is admitted that with only the above data calculation of the absolute minimum eutectic mixture is impossible. It should also be understood that the measurements, while as accurate as possible considering the apparatus and the chemicals available, are not exact. Exact determination of these curves should be carried out by physico-chemical methods, using the purest chemicals and the most sensitive of potentiometers. The experimental work in this field satisfactorily supplied the information that was sought.

The first work in this field was directed towards determining the cooling curve of the lithium fluoride-potassium fluoride system. A furnace capable of developing a temperature of one thousand degrees was employed in all measurements. A thermocouple was inserted through the insulation of the cover of the furnace into the fluoride mixture whose cooling curve was to be measured. Since the mixture of the fluorides reacts with the metal composing the thermocouple, a copper sheath made from copper tubing was employed so that no fluoride could come in contact with the

thermocouple. A 100-cc. nickel crucible served to hold the melt, and in all cases approximately 200-gms. of melt was employed to determine the cooling curves.

The cooling curves for all compositions of the system LiF-KF indicated the existence of a eutectic mixture at about 450°, the indication being the usual horizontal section of the cooling curves and the existence of only one break or turning point besides the horizontal section..

Mole % LiF	1st break	horizontal section
90%	.0267*	.0186*
80%	.0238	.0188
50%	.0258	.0190
50%	.0254	.0187
60%	.0210	.0187

*Potential developed with Chromel-Alumel thermocouple. Cold junction at 0°. Expressed values given in volts.

Proper construction of a freezing point diagram indicated that the eutectic has the approximately the composition 70 mole percent lithium fluoride and 30 mole percent potassium fluoride.

Investigation of the lithium fluoride-potassium fluoride system showed that the eutectic mixture has a melting point of over 600° . A composition of 70 mole percent LiF, 26 mole percent KF, and 4 mole percent NaF was decided on for the working mixture.

Two hundred grams of melt of the above composition was placed in a nickel crucible and a stream of boron trifluoride directed into the melt keeping the fused mass at a temperature as near to the melting point as possible. The boron trifluoride was prepared by the ^{inter-}action of 100 grams B_2O_3 , 200gms. CaF_2 , and 500-cc. of concentrated sulfuric acid. The preparation was very satisfactory. The passage of the boron trifluoride into the melt was readily observed. When viewed under strong light a stream of particles is noticed to form at the mouth of the boron trifluoride tube, slowly sinking towards the bottom. The initial mixture of fluorides when cooled appeared like any other fused mass, but the boron trifluoride-alkali fluoride melt (borofluoride) when cooled has a very vitreous, milky appearance. It has a high luster and resembles white paint when dry.

It took about an hour to run in all the boron tri-fluoride, as indicated by the fact that the bubbles rise to the surface when the supply tube is run below the surface of the melt. Immersion of the tube during the first hour resulted only in complete absorption.

The temperature of the mixture proved to be above four hundred degrees, indicating that a mixture of alkali borofluoride had little likelihood of being successfully used for the electrolytic production of fluorine. It was decided, however, to conduct a trial electrolysis. A small all-nickel generator was employed. The container acted as the cathode and a nickel rod, insulated from the cover, passed down into the melt. The electrolysis was carried out for one hour with a current of 15 amperes. The potential drop across the cell was about 15 volts. The electrolysis was discontinued and the cell disassembled. The anode showed extreme attack, indicating that the fluorine reacted with the anode as soon as it was produced. The container showed little or no wear. It could not be determined what metal or metals had been liberated at the cathode. However, since the mixture of alkali borofluorides conducts well, and since the only positive elements present were

potassium and boron it is believed that the electrolysis results in the decomposition of the boron trifluoride.

CONCLUSIONS

Fluorine can be produced by the electrolysis of a solution of potassium fluoride in anhydrous hydrogen fluoride in which the mole proportions correspond to the formula $KF \cdot 3HF$. The container may be constructed of copper, but the anode should be made of nickel. The preparation of fluorine by this process is far from satisfactory, due to the vapors of hydrogen fluoride and the explosive character of mixtures of hydrogen and fluorine which may be formed.

The method of producing fluorine based upon the electrolysis of fused mixtures of alkali borofluorides is unsuccessful, since at the temperature of operation, fluorine is far too active and reacts with the metallic anode.

On the whole the production of fluorine is still a problem that has been far from successfully solved.

A real need for fluorine exists and investigation along these lines should be intensified.

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