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The preparation of elementary fluorine and its reactions with certain organic compounds

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THE PREPARATION OF ELEMENTARY FLUORINE AND ITS REACTIONS WITH CERTAIN ORGANIC COMPOUNDS

BY

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A

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INTRODUCTION

This work had two main objectives: (1) The construction of an electrolytic cell for the production of fluorine, (2) the preparation of some organic compounds containing fluorine.

This research was undertaken because of the growing importance of fluorine chemistry, particularly in the field of organic chemistry. Due to the extreme activity of fluorine, it is theoretically possible to prepare many times more fluorine-containing organic compounds than there are known organic compounds today. It has been predicted[1] that fluorine-containing products will be developed to include new and useful dyes, plastics, pharmaceuticals, lubricants, tanning agents, metal fluxes, fumigants, insecticides, germicides, fire extinguishers, solvents, fireproofing compounds, heat transfer media, and other beneficial products. Use may also be made of the volatility of certain fluorides to effect separations of contaminating elements from ores by volatilization.

The electrolytic cell used in this work for the generation of fluorine was similar to cells described in the literature[2]. Fluorine was produced by the electrolysis

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(1) McBee, E. T., Ind. Eng. Chem., Vol. 39, no. 3, p. 237 (1947).

(2) Cady, G. H., Rogers, D. A., and Carlson, C. A., Ind. Eng. Chem., Vol. 34, p. 443 (1942).

of a solution having the approximate composition KF·2HF, at temperatures just above its melting point of about 70° C.

The most useful method thus far reported for introducing fluorine into an organic molecule is by the use of metal carriers(3). In particular, antimony trifluoride, in the presence of a pentavalent antimony salt has found wide application, in what is known as the Swarts reaction(4). This has suggested an investigation of the fluorinating activity of such related fluorides as cobalt trifluoride, manganese trifluoride, silver difluoride, and mercuric fluoride.

To investigate the fluorinating properties of these metal fluorides, it was decided to attempt to bring about reactions with 2, 4-dichlorophenoxyacetic acid. Unsubstituted phenoxyacetic acid has only slight effect on the growth characteristics of plants, but when chlorine is added to the ring nucleus at the ortho and para positions, the molecule becomes highly activated(5). 2, 4-Dichlorophenoxyacetic acid is rapidly gaining widespread use as a selective plant growth regulator and, in larger concentrations, as a differential herbicide. Bromo-substituted homologs have been reported(6), but there seems to be no report

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(3) Henne, A. L., "Organic Reactions", Vol. II, p. 49-94, N. Y., Wiley, 1944.

(4) Swarts, F., Bull. Acad. Roy. Belg., Vol. 35, p. 375 (1898).

(5) Gilbert, F. A., Chem. Rev., Vol. 39, p. 199 (1946).

to date of fluoro-derivatives. It would be of interest to investigate the substitution of fluorine atoms into the ring nucleus.

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(6) Zimmerman, P. W., Ind. Eng., Chem., Vol. 35, p. 596 (1943)

REVIEW OF LITERATURE

The Generation of Fluorine

The literature on this subject is extensive, even though the preponderance of work has been done in the past five years. The electrolytic cells thus far described for the production of fluorine appear to conform to one of two basic designs: (1) A U- or V-shaped container supporting an electrode in each arm, or (2) A pot provided with a diaphragm which serves to separate the anode and cathode products, but permits free circulation of the electrolyte. The electrolyte has almost always been an alkali fluoride in combination with varying amounts of anhydrous hydrogen fluoride. None of the generators described was capable of producing pure fluorine; the product always contained a few per cent of such contaminants as hydrogen fluoride, air, oxygen fluoride, carbon fluorides, and possibly other gases.

Moissan[7] was the first to describe a successful fluorine generator. His apparatus consisted essentially of a platinum U-tube closed with fluorite stoppers and equipped with side-arm delivery tubes. The anode, at which the fluorine was liberated, was made of a highly resistant platinum-iridium alloy, but even this was seriously corroded. The electrolyte was a solution approximately 30 per cent potassium bifluoride in anhydrous hydrogen fluo-

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(7) Moissan, H., Compt. rend., Vol. 103, p. 202, (1886).

ride maintained at a temperature between -23° and - 50° C.

Moissan's cell, although successful, possessed the following disadvantages: high initial cost, difficult of operation, and low resistance of the expensive anode to the fluorine generated.

The next significant development in fluorine generation was reported in 1919 by Argo, Mathers, Humiston, and Anderson(8). Their cell was designed to operate at temperatures of 250 - 300° C. with an electrolyte of potassium bifluoride. The apparatus consisted essentially of a cylindrical copper vessel, open to the air and surrounded by electrical resistance coils to maintain the temperature required to melt the electrolyte. The anode was a heavy graphite rod, suspended in the electrolyte by means of a copper bolt, and surrounded by a cylindrical copper diaphragm, closed top and bottom to provide a gas-tight anode compartment. A fluorine outlet tube was provided near the top of this compartment, and a series of saw-slots were located near the bottom to facilitate movement of the electrolyte. The copper anode connection was insulated from the diaphragm by means of a packing of powdered fluorspar supported on a fluorite ring. The copper vessel which served as the cathode was also insulated from the diaphragm.

The cell of Mathers et al. possessed the advantages of

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(8) Argo, W. L., Mathers, F. C., Humiston, B., and Anderson, C. O., Trans. Am. Electrochem. Soc., Vol. 35, p. 335 (1919).

being rugged and inexpensive, and it did not require a highly skilled operator. Its current efficiency of 70 per cent was about twice that of the Moissan cell. The principal disadvantages noted were: recurring anode polarization, and solution of the copper of the diaphragm due to the high temperature of the electrolyte.

Whearty's fluorine cell [9] resembled the Mathers cell except that magnesium replaced the copper as a structural metal. The principal innovation in the Whearty system was the electrolyte, which consisted of a eutectic of 35 per cent sodium bifluoride and 65 per cent potassium bifluoride, melting at 170° C. The cell was wound with nichrome heating elements to obtain this temperature. In operation, the Whearty cell was comparable to that of Mathers.

The cell of Dennis, Veeder, and Rochow[10] was reported at about the same time as Whearty's and differed in that it was constructed in a V-shape. The anode was of graphite and the cell was designed to operate at high temperatures. Electrical resistance windings were used to provide the temperatures required. This cell was reported to operate at efficiencies of 45 to 76 per cent.

Bockemüller's generator[11] also was designed to elec-

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(9) Whearty, Jr., J. F., J. Phys. Chem., Vol. 35, p. 3121 (1931).

(10) Dennis, L. M., Veeder, J. M., and Rochow, E. G., J. Am. Chem. Soc., Vol. 53. 3263 (1931).

(11) Bockemüller, W., Ann., Vol. 506, p. 20 (1933).

trolyze potassium bifluoride at temperatures of 250 - 270° C. He employed the diaphragm-type cell with a graphite anode and an insulated cathode of copper. This cell was not open to the atmosphere and operated at current efficiencies of 70 to 85 per cent.

The fluorine generator described by Cady, Rogers, and Carlson[12] possessed one essential difference from the others in that it operated at a medium temperature of 75° C. and employed a nickel anode. This cell was surrounded by a steam jacket and contained a slat-type, jointed diaphragm which readily permitted the passage of electrolyte. An innovation was the provision of a hydrogen fluoride inlet to effect the constant regeneration of electrolyte.

The Cady cell was free of polarization difficulties, and possessed the obvious advantages of operating at a convenient and economically maintained temperature. The lower temperatures also resulted in markedly less corrosion than common in high temperature cells. The principal disadvantage was the the open construction permitted the electrolyte to absorb moisture from the air, when the cell was not in operation.

Another generator worthy of detailed consideration is that of Miller and Bigelow[13]. This cell was reported

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(12) Cady, G. H., Rogers, D. A., and Carlson, C. A., Ind. Eng. Chem., Vol. 34, p. 443 (1942).

(13) Miller, W. T., and Bigelow, L. A., J. Am. Chem. Soc., Vol. 58, p. 1585 (1936).

to have produced fluorine of 94.4 - 99.0 per cent purity by operating under rigorously anhydrous conditions. The electrolyte was molten potassium bifluoride. The apparatus consisted of a heavy cast-nickel, U-shaped vessel, provided with polished flanges at both ends, and equipped with polished cast-nickel caps, made gas-tight by lead gaskets and held firmly in place with steel bolts. The graphite electrodes were screwed to nickel rods, which passed through the end caps, and were held in place by a resistant insulating packing made from powdered fluorspar and portland cement. The end caps were also provided with adequate exit tubes for the hydrogen and fluorine, respectively. A thermometer well extended directly into the body of the casting. The entire unit was contained in a rectangular box-shaped electric heater. If the electrolyte was painstakingly prepared in anhydrous form, this cell operated smoothly to produce high quality fluorine, using a current of 5 amperes and a potential drop of 18-20 volts.

Bigelow states that this cell possessed the following advantages: (1) Contamination of the anode gas by oxygen and oxygen fluoride was completely eliminated, (2) It was rugged, and could be adapted reasonably well to large-scale production, (3) It was almost unaffected by corrosion on account of a protective surface coating on the nickel, (4) It operated for long periods of time with smoothness and no trace of violent reactions of any kind. As disadvantages, he lists: (1) A tedious dehydration process for pre-

paring the electrolyte, (2) Infiltration of the electrolyte between the nickel and the graphite, causing the electrodes to crack at times, (3) The formation of salt bridges over the insulation, resulting in a partial or complete short circuit, (4) The possibility that the exit tubes be clogged with frozen melt.

Some fluorine cells appearing more recently in the literature are those described by Schumb, Young, and Radimer[14], Pinkston[15], McBee and Bechtol[16], and Miller, et al.[17]. A study of these papers seems to indicate that the following are the desirable features to be incorporated in a cell for the electrolytic generation of fluorine: (1) A diaphragm-type cell, either cylindrical or box-shaped, closed to the atmosphere, (2) Operating temperatures of 70 - 100° C., these temperatures to be maintained by means of a steam jacket around the body of the cell, (3) Steel, stainless steel, or monel metal as a construction material for the cell body, cathode, and fittings, (4) monel metal, copper, or nickel screen for a diaphragm, (5) cathode separate from the cell body to allow free circulation of the electrolyte, (6) Anodes of graphite or copper-impregnated graphite,

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(14) Schumb, W. C., Young, R. C., Radimer, K. J., Ind. Eng. Chem., Vol. 39, No. 3, p. 244 (1947).

(15) Pinkston, J. T., ibid., p. 255.

(16) McBee, E. T., and Bechtol, L. D., ibid, p. 380.

(17) Miller, W. T., Ehrenfeld, R. L., Phelan, J. M., Prober, M., and Reed, S. K., ibid., p. 401.

(7) Electrolyte of fused anhydrous salt of the approximate composition $KF \cdot 2HF$ with 1.0 to 1.5 per cent lithium fluoride added to prevent polarization, (8) provision for constant regeneration of electrolyte by addition of anhydrous hydrofluoric acid.

The Fluorination of Organic Compounds

As might be expected, the pioneer work in the field of organic fluorine compounds dealt principally with attempts at direct fluorination. This work was initiated by Moissan[18] and his pupils. They found in general that the reactions were difficult to control, violent, and often explosive. In many cases, the organic molecule was disrupted, and the only products of the reaction appeared to be carbon tetrafluoride, hydrogen fluoride, and free carbon. Moissan found fluorine to be so reactive that a powerful explosion resulted when he attempted to react solid methane with liquid fluorine at -187° C.

The development of organic fluorine chemistry has proceeded along two lines: (1) Direct fluorination and (2) Indirect fluorination. Although much important work has been done in methods of direct fluorination, attention will be directed here mainly to the indirect methods.

Indirect fluorination reactions of three general types have been reported:

1. Substitution of hydrogen or halogen by means of inorganic fluorides:

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(18) Moissan, H., Compt. rend., Vol. 110, pp. 276, 951 (1890).

$$RH + 2MF_x = RF + 2MF_{x-1} + HF$$

$$RX + MF = RF + MX$$

2. Addition of hydrogen fluoride to unsaturated molecules:

$$RCH{=}CHR' + HF = RCH_2\text{-}CHFR'$$

$$RC{\equiv}CR' \xrightarrow{HF} RCF{=}CHR' \xrightarrow{HF} RCF_2\text{-}CH_2R'$$

3. Replacement of the hydroxyl group of alcohols:

$$ROH + HF \rightleftharpoons RF + HOH$$

Of these three, the first method has proven to be by far the most useful.

Swarts[19] was among the first to report fluorinations by halogen replacement using metal fluorides, and did considerable work using the fluorides of antimony. Fluorination using antimony trifluoride alone is generally not vigorous and seldom results in good conversions. The addition of a small quantity of pentavalent antimony salt, usually the trifluorodichloride, permits the exchange of halogen atoms to proceed to completion. The quantity of pentavalent salt added can act as a regulator of the reaction.

Predominant in the literature of this country is the work of Henne and co-workers, beginning in 1932. Reports of his work on the synthesis of a large number of aliphatic and some aromatic fluorides appear at frequent intervals and are well summarized in a report of 1944 (Organic Reactions, Vol II)[20]. Although Henne has investigated both

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(19) Swarts, F., op. cit., p. 2.

(20) Henne, A. L., op. cit., p. 2.

direct methods of fluorination, most of his work involved indirect methods, principally halogen replacement by means of inorganic fluorides. Reactions were reported between organic halides and the following inorganic fluorides: antimony trifluoride, potassium fluoride, argentous fluoride, zinc fluoride, mercurous fluoride, and mercuric fluoride. Henne considers these reactions to be metathetical and does not view the inorganic fluoride as a metal "fluorine carrier". Apparently no chlorine is evolved in the reactions with organic chlorides.

Ruff[21] discussed a number of high-valence metal fluorides, prepared only by use of elementary fluorine, which he showed to be powerful oxidizing agents. Manganese trifluoride, cobalt trifluoride, and silver difluoride were among those discussed.

It is unfortunate that due to war-time security regulations much of the research on both direct and indirect fluorinations was not reported in the literature until this investigation was well under way. Although there is no report of the fluorination of a partially halogenated aromatic nucleus which also contains an -OR group, a number of papers[22],[23],[24] have recently appeared which have

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(21) Ruff, O., "Die Chemie des Fluors", p. 50, Berlin, Julius Springer, (1920).

(22) Benner, R. G., et al., Ind. Eng. Chem., Vol. 39, no. 3, p. 329 (1947).

(23) Miller, W. T. et al., ibid., p. 333.

(24) Bigelow, L. A., Tompson, R. Y., and Tarrant, P., ibid., p. 360.

some bearing on this work, particularly the reports of investigations carried out by Fowler and co-workers[25],[26] and those conducted in collaboration with McBee[27],[28]. In these papers the following metallic fluorides were discussed: CoF_3, MnF_3, CeF_4, PbF_4, BiF_5, CrF_4, CrF_5, and HgF_2. From the positions of silver and cobalt in Table I[26] it was predicted that some of the other metals lying just below them in oxidizing power might yield fluorinating agents of less activity. Manganese trifluoride and ceric fluoride were shown to be comparable to cobalt trifluoride as fluorinating agents; but the fluorides of lead, bismuth, mercury, and chromium could not be successfuly applied in existing apparatus. The general consensus of these papers was that cobalt trifluoride is quite satisfactory for fluorinating hydrocarbons. It further appeared that silver difluoride was more effective than cobalt trifluoride for chlorine replacement.

Fluorination by means of metal carriers is less drastic and therefore more easily controlled than fluorination by elementary fluorine. The general mechanism of such reactions is given as follows: First, the fluorination of the

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(25) Fowler, R. D., et al., ibid., p. 292.

(26) Fowler, R. D., et al., ibid., p. 343.

(27) McBee, E. T., et al., ibid., p. 298.

(28) McBee, E. T., et al., ibid., p. 310.

TABLE I. HALF CELL REACTIONS AND POTENTIALS[26]

Couple	E^o
$2HF = F_2 + 2H^+ + 2e^-$	-3.03
$2F^- = F_2 + 2e^-$	-2.85
$Ag^+ = Ag^{++} + e^-$	-1.98
$Co^{++} = Co^{+++} + e^-$	-1.84
$Bi^{+++} = Bi^{+++++} + 2e^-$	-1.7 (approx.)[a]
$Pb^{++} = Pb^{++++} + 2e^-$	-1.69
$Ce^{+++} = Ce^{++++} + e^-$	-1.61
$Mn^{++} = Mn^{+++} + e^-$	-1.51
$7H_2O + 2Cr^{+++} = Cr_2O_7^{--} + 14H^+ + 6e^-$	-1.36
$Hg_2^{++} = 2Hg^{++} + 2e^-$	-0.910
$Fe^{++} = Fe^{+++} + e^-$	-0.771
$2H_2O + HAsO_2 = H_3AsO_4 + 2H^+ + 2e^-$	-0.559
$Cu^+ = Cu^{++} + e^-$	-0.167
$Sn^{++} = Sn^{++++} + 2e^-$	-0.15
$H_2O + H_3PO_3 = H_3PO_4 + 2H^+ + 2e^-$	0.20

[a]Estimated; Latimer gives a value of about -1.59 for the reaction $Bi_2O_3 = Bi_2O_5 \quad 4e^-$.

lower metallic fluoride to the higher:

$$MF_L + \left(\frac{H-L}{2}\right) F_2 \longrightarrow MF_H$$

and, second, the replacement of hydrogen or halogen in the organic molecule with fluorine by the higher fluoride:

$$-CH_2- + \left(\frac{4}{H-L}\right) MF_H \longrightarrow -CF_2- + 2HF + \left(\frac{4}{H-L}\right) MF_L$$

or:

$$-CHX- + \left(\frac{1}{H-L}\right) MF_H \longrightarrow -CHF- + \tfrac{1}{2}Cl_2 + \left(\frac{1}{H-L}\right) MF_L \ .$$

The spent fluoride is then regenerated with elementary fluorine.

Recent techniques of fluorination reactions are summarized, including the use of halogen fluorides, in Chemical Industry[29].

(29) Editorial Staff Report, Chem. Ind., Vol. LIX, no. 6, p. 1006 (1946).

It was not considered to be within the scope of this work to make a complete review of the literature regarding the use of phenoxy compounds as plant growth regulators. Sufficient search of the literature was carried out to ascertain that fluorine-substituted phenoxy compounds had not been previously investigated or prepared.

Phenoxyacetic acid as such is but slightly active, but halogen-substituted phenoxy compounds are activated according to the positions and the number of substituted groups in the nucleus of the molecule. The shifting of only a single chlorine in the ring will greatly alter the effectiveness of the compound,(30), but Snyder(31) states that 2,4-dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid are almost equally effective, and 2,4,6-tribromophenoxyacetic acid will kill poison ivy.

Techniques of preparing 2,4-dichlorophenoxyacetic acid were readily derived from directions for the preparation of phenoxyacetic acid (32) and a description of the manufacture of 2,4-D(30).

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(30) Tukey, H. B., The Scientific Monthly, Vol. LXIV, no. 2, p. 93 (1947)

(31) Snyder, Chemurgic Digest, Vol. 4, p. 188 (1945).

(32) Shriner, R. L., and Fuson, R. C., "Identification of Organic Compounds", 2nd ed., J. Wiley and Sons, N. Y., p. 174 (1940).

THE PREPARATION OF ELEMENTARY FLUORINE

Construction of the Electrolytic Cell

A study of the literature on electrolytic generation of fluorine seemed to indicate that the medium temperature diaphragm-type of cell would be the most favorable for the laboratory generation of fluorine. Copper was chosen for the material of construction because of its low cost, workability, and resistance to corrosion.

Figure 1 shows the major components of the fluorine cell. A heavy jacketed copper pot, 6½ inches high by 6 inches in diameter (all measurements internal dimensions), served as cathode and container for the electrolyte. Two holes were drilled in the wall of the surrounding jacket, near the top and bottom respectively, and 3/8 inch diameter copper nipples were soldered into these holes to provide a means of entrance and exit for the steam and hot water into and out of the surrounding steam jacket. The bottom nipple was extended into the steam jacket to a point just beneath the center of the bottom of the inside pot containing the electrolyte, so that the steam would enter the jacket at a point where it could produce uniform heating. Rubber hoses (not shown in figure 1) were provided for the purpose of conducting either steam, or water, or a mixture of the two to the steam jacket. These rubber hoses were so provided with tees and pinch-cocks that any of the following heating or cooling arrangements may be utilized: (1) Steam alone, entering at the bottom and exhausting at

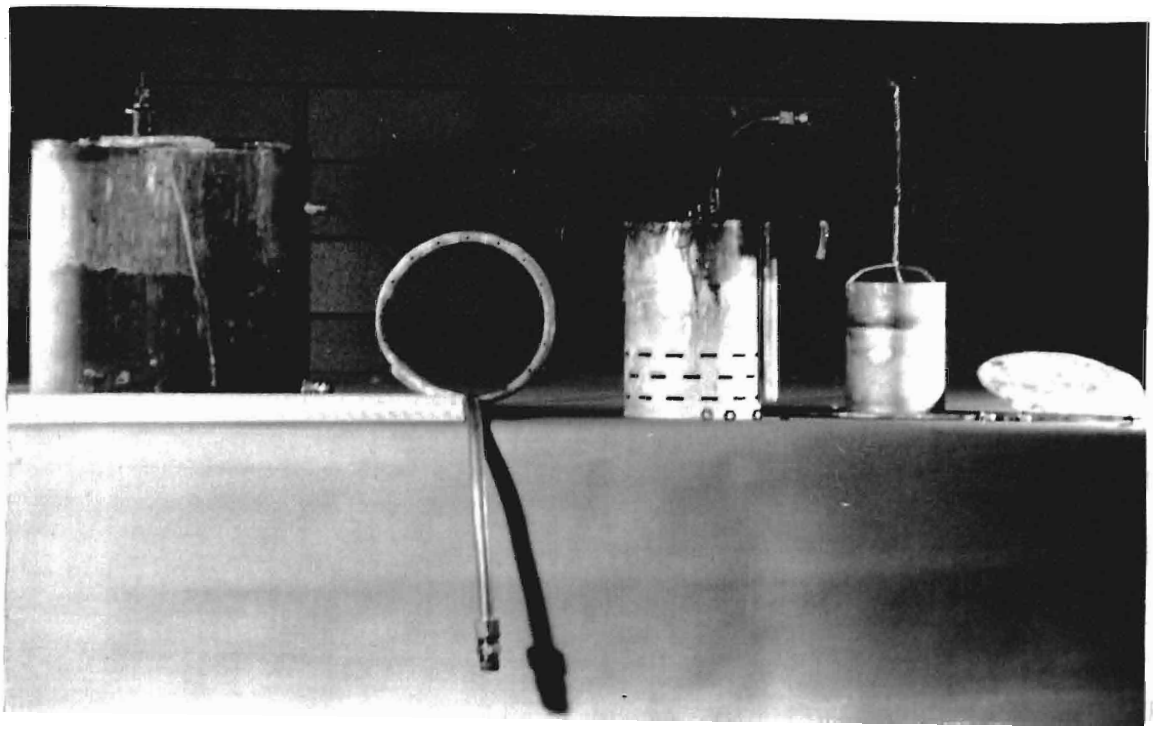

Figure 1. THE PARTS OF THE FLUORINE GENERATOR

The cell body and heating jacket unit is on the left, showing the cathode binding post at the top and the two steam-water fittings on the right side of the jacket. Next is the hydrogen fluoride delivery tube, then the diaphragm - anode compartment, the nickel anode, and the diaphragm bottom cover is on the right. In front are the diaphragm connecting bolts and nuts; these bolts serve to hold the diaphragm bottom cover in place during operation of the cell.

the top; (2) Steam alone, entering at the top and leaving at the bottom; (3) Cold water alone entering at the top and leaving at the bottom, or (4) vice-versa; (5) Any mixture of steam and water (hot water) flowing either upward or downward through the jacket. An electrical bind-

ing post for the cathode connection was provided at the top of the electrolyte container.

Four feet of 3/8 inch copper tubing, bent at the bottom into a single helix, and drilled with a number of evenly-spaced 1/8 inch holes around the helix comprised the hydrogen fluoride delivery tube (figure 1). This tube was closed at the lower end before bending by turning on a lathe with a ball-head tool at high speed. At the upper end it was connected to the hydrogen fluoride line by means of brass compression fittings and a brass coupling. In operation, the hydrogen fluoride delivery tube extended below the surface of the electrolyte and could be used to replenish the hydrogen fluoride as needed.

The diaphragm, anode compartment and bottom cover (figure 1) were constructed of 3/32 inch sheet copper. The diaphragm was made into a cylinder, 4 inches in diameter, the edges joined by an overlap joint. Three rows of slots, ½ inch apart, staggered, were punched around the bottom of the diaphragm. Each slot was ½ inch long, 1/8 inch wide, and the slots are ½ inch apart. The bottom row of slots was ½ inch from the bottom of the diaphragm.

The diaphragm bottom cover was also made from sheet copper by cutting a disc 5 inches in diameter. Four 1/8 inch copper rods were made to hold the bottom cover in place by belting it to the top cover.

The top cover was so designed that parts of it extended over the top edge of the electrolyte container and

thus served to suspend the diaphragm and anode compartment in the electrolyte.

A hole was drilled off-center in the top cover to receive the fluorine outlet tube of 3/8 inch copper tubing. Because a number of previous workers(33), (34), (35) reported foaming of the electrolyte, a baffle was soldered in place just below the opening of the fluorine tube in an effort to prevent the possibility of any electrolyte getting into the fluorine tube and plugging it.

A ½ inch hole was drilled in the center of the top cover to receive a short nipple which served to support the anode. The copper lead to the anode was passed through this opening and held in place with portland cement.

The thermometer well, which was suspended beside the diaphragm, was made from a short piece of 3/8 inch copper tubing by closing the bottom end on the lathe in the same manner that the bottom of the hydrogen fluoride delivery tube was closed. The thermometer well was partially filled with cylinder oil to provide a medium of heat transfer to the thermometer. All joints around the top of the anode compartment were soldered.

Two anodes were employed with this cell. The first

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(33) Argo, et al. op. cit., p. 5.

(34) Dennis, Veeder, and Rochow, op. cit., p. 6.

(35) Simons, J., J. Am. Chem. Soc., Vol. 46, p. 2175 (1942)

anode was cut from a block of carbon obtained from the Department of Metallurgy of the School of Mines. It was cut into the shape of a rod four inches long and three inches in diameter. A hole was drilled into the top of the anode and the anode lead, a rod of 1/8 inch solid copper, was driven into this hole.

The second anode (figure 1) was constructed from 3/32 inch sheet nickel, fastened into the shape of an open cyl-

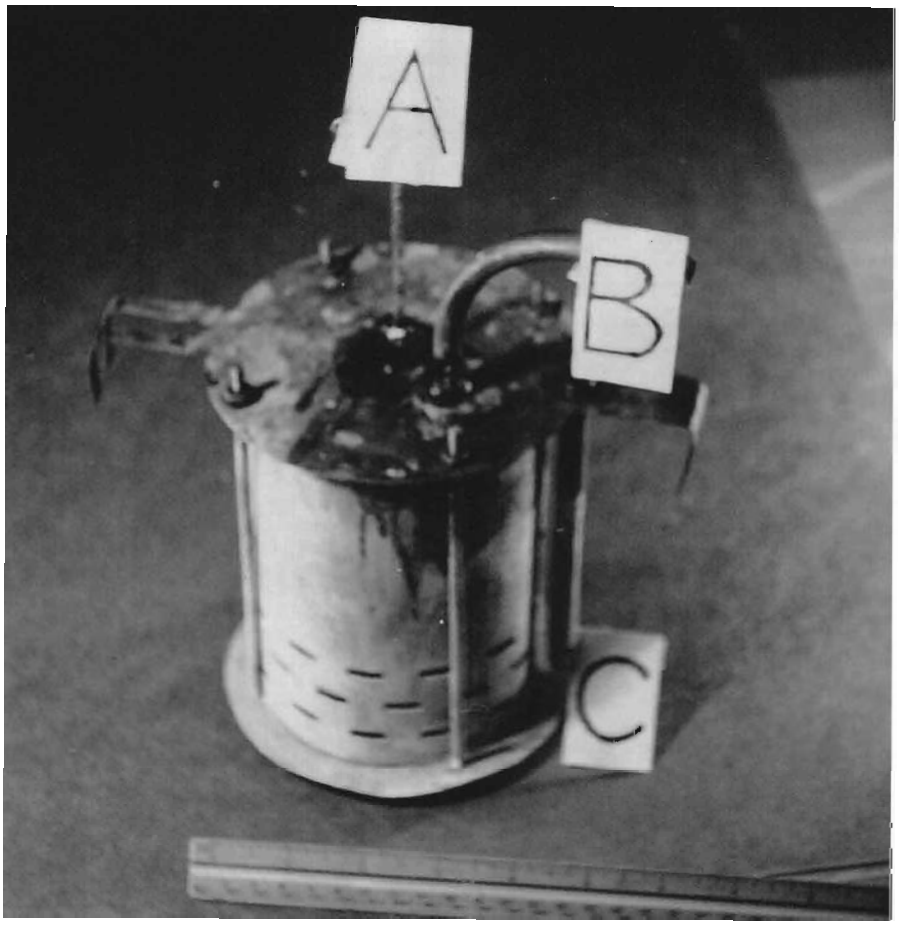

Figure 2. THE DIAPHRAGM COMPLETELY ASSEMBLED.

A, the anode lead; B, the fluorine outlet;
C, the thermometer well.

inder, four inches long by three inches in diameter. The anode lead was copper, wired into holes drilled in the upper part of the anode. Figure 2 shows the diaphragm and anode compartment assembled, just as when in operation in the cell.

The distance between electrodes in this fluorine cell is 1.45 inches. When operating at a current of 10 amperes, with the cell 2/3 full of electrolyte, current densities are at the following values: cathode, 0.232 amperes per square inch; anode, 0.264 amperes per square inch.

Preparation of the Electrolyte

Almost all of the fluorine generators thus far described in the literature use as an electrolyte a solution of potassium bifluoride in varying amounts of hydrogen fluoride. In general, three different ranges of concentration have been found satisfactory. These become evident upon study of figure 3[36], a diagram of the system potassium fluoride - hydrogen fluoride with some superimposed vapor pressure isobars. The solid line represents the freezing point curve and the dashed lines represent, respectively, hydrogen fluoride vapor pressures of 5.0 cm., 10.0 cm., and 25.0 cm. of mercury. Since hydrogen fluoride constitutes a chief contaminant of the fluorine generated, the most desirable ranges of electrolyte composition are those wherein the electrolyte is a liquid with a low vapor pressure. The three concentration ranges that

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(36) Cady, Rogers, and Carlson, op. cit. p. 2.

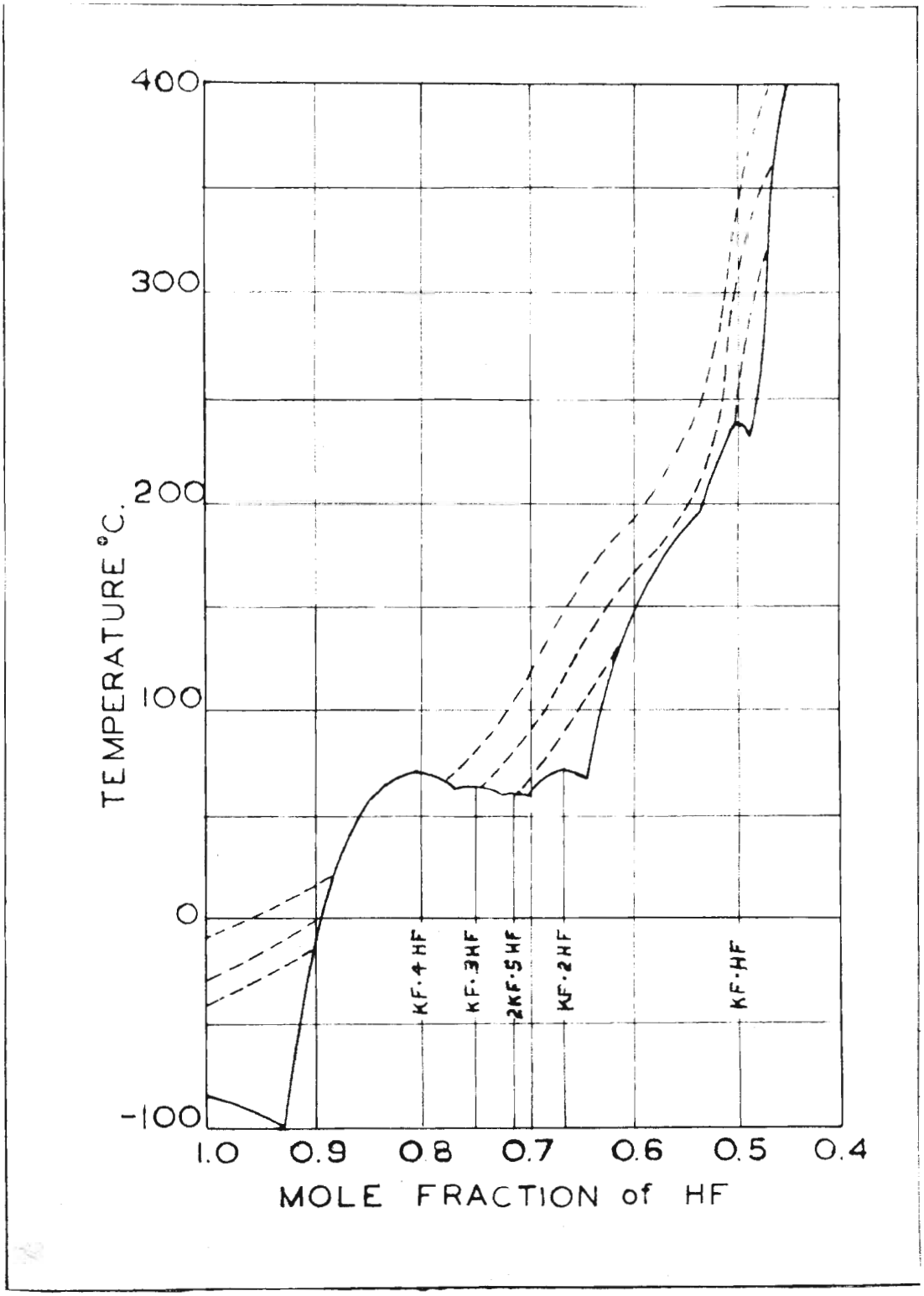

Figure 3. DIAGRAM OF THE SYSTEM POTASSIUM FLUORIDE-HYDROGEN FLUORIDE

Solid line represents freezing points, dashed lines, vapor pressures; the highest curve, 25 cm., the middle curve, 10 cm., the lowest curve for 5 cm. of mercury.

would permit a liquid electrolyte with a vapor pressure less than 5.0 cm. of mercury (arbitrarily chosen) are: (1) Above 0.9 mole fraction of HF, at temperatures in the region of -50° C., (2) The approximate composition KF·2HF, within a temperature range of 70 - 110° C., (3) The approximate composition KF·HF, at temperatures from 240 to 320 degrees C.

Since the intermediate composition (approximately KF·2HF) permits the most convenient working temperatures, it was chosen for this investigation. Attempts were made to prepare this electrolyte by three slightly different methods.

The first method employed was given by Booth(37). To 2 pounds of pure "Baker's Analyzed" potassium bifluoride, $KHF_2 \cdot 2H_2O$, in a copper pot, was added one pound of B. and A. assay grade aqueous (48%) hydrofluoric acid. This provided about 37 per cent excess of hydrofluoric acid to allow for evaporation of the hydrogen fluoride during dehydration. The temperature was now raised very slowly to the boiling point, as directed, in order to evaporate the water, but after holding the temperature at or just below the boiling point for about an hour, it was noticed that corrosion of the copper pot, with consequent contamination of the electrolyte, was appreciable and the heating was discontinued. The container of potassium bifluoride and hydrofluoric acid was next placed in a water bath and a bundle of four graphite electrodes, fastened to allow space be-

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(37) Booth, H. S., Inorganic Syntheses, Vol. I, p. 136, McGraw-Hill, N. Y., (1939).

tween them was lowered into the electrolyte mixture. With the copper container acting as a cathode, a current of 5 to 10 amperes was passed through the mixture, until fluorine began to form at the anode, as evidenced by a crackling noise and the odor of fluorine.

About ten hours were required to remove the water by electrolysis. As the solution became more concentrated, the water bath was removed and the temperature was maintained just above the melting point of the electrolyte. The graphite anodes were appreciably attacked during the process. This was believed due to a sufficiently porous structure of the electrode to permit the aqueous electrolyte to permeate the graphite, where any gas liberated within the body of the anode would cause disintigration of the anode. This action was not nearly as severe in the case of anhydrous electrolyte.

The quantity of reagents in stock was inadequate to prepare sufficient electrolyte for continued operation; the first electrolyte was soon consumed. Some difficulty was experienced in obtaining additional potassium bifluoride; therefore, it was decided to prepare the $KF \cdot 2HF$ from stick potassium hydroxide and aqueous hydrofluoric acid, both of which were in stock in sufficient quantity.

Following is the second method employed to prepare the electrolyte: Two pounds of Mallinckrodt 85% analytical grade potassium hydroxide was added to 800 ml. of dis-

tilled water and the mixture was heated to facilitate solution. Four pounds of aqueous (48%) hydrofluoric acid were placed in a wax-coated three liter beaker set in a water bath and equipped with a mechanical stirrer. The concentrated potassium hydroxide solution was placed in a one-liter separatory funnel suspended above the beaker of hydrofluoric acid and the stop-cock was adjusted to permit the potassium hydroxide to run into the hydrofluoric acid at a rate of approximately two drops per second, while the hydrofluoric acid was stirred at a rate of about one revolution per second. After all of the potassium hydroxide solution was added, electrodes were inserted into the solution and a current of 7 - 10 amperes was passed at a potential of approximately 8 volts to decompose all the water present.

Because of the experience with disintigrating graphite anodes in the preparation of the first electrolyte, nickel electrodes were used in the second method. This procedure required about seventy-two hours of electrolysis to remove all the water present. As the melting point of the electrolyte increased due to removal of water, the electrolyte was removed from the wax-coated beaker and placed in a copper pot as before, so that the temperature could be maintained just above the melting point of the electrolyte.

The third method of preparing the electrolyte was also

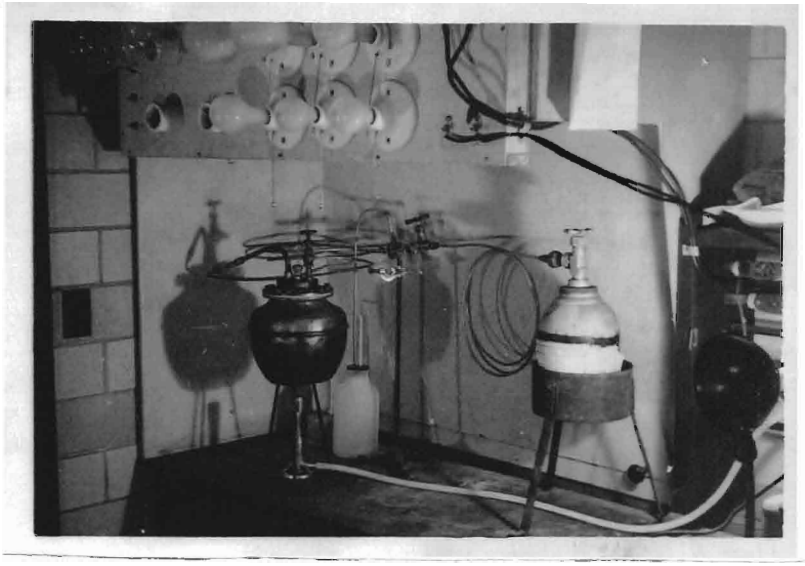

Figure 4. PREPARATION OF THE ELECTROLYTE, FIRST STAGE.
Anhydrous hydrofluoric acid, from the cylinder on the right was admitted to the autoclave on the left, which was heated by a Fisher burner. A vacuum break with $CaCl_2$ drying column in the HF line, may be seen behind the burner, partially obscured by the autoclave.

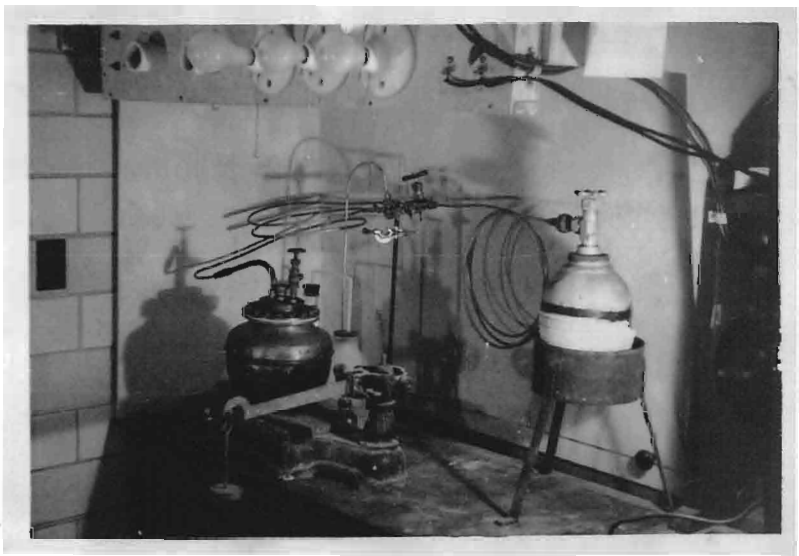

Figure 5. PREPARATION OF THE ELECTROLYTE, SECOND STAGE.
After the bulk of the hydrofluoric acid had been added, the autoclave was given a preliminary heating and placed on the scale to receive the remainder of the hydrofluoric acid.

based on a procedure given by Booth[38], and is the method recommended. Three pounds of anhydrous potassium bifluoride, obtained from the Harshaw Chemical Company was placed in a small brass autoclave and melted with a Fisher burner. The autoclave cover was then fastened into place and anhydrous hydrofluoric acid, also obtained from the Harshaw Chemical Company in a metal cylinder was introduced beneath the surface of the molten potassium bifluoride. The anhydrous hydrofluoric acid was readily absorbed by the potassium bifluoride. After the hydrofluoric acid has been added slowly for several hours, the addition was stopped, and the autoclave and contents was found to have increased in weight by 0.6 pounds. The autoclave was then heated several degrees above the melting point of the electrolyte it contained, and placed upon a small platform scale for the addition of the remainder of the hydrofluoric acid. The weights on the scale were set for the addition of a total of 0.8 pounds of anhydrous hydrofluoric acid, and the addition of anhydrous HF was stopped when the balance was brought into equilibrium. The melting point of this electrolyte was found to be 73° C.

The third method was found to be the most convenient way of preparing the electrolyte. The total operation required only seven hours. After the electrolyte had been prepared, a carbon electrode was inserted into the melt,

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(38) Booth, H. S., Inorganic Syntheses, Vol. I, p. 143, McGraw-Hill, N. Y., (1939).

and, with the brass autoclave serving as a cathode, a current of 7 amperes was passed through the electrolyte at a potential of 8 volts to determine whether the electrolyte contained any water. It was found to be practically anhydrous, for fluorine was evolved almost immediately.

Operation of the Electrolytic Cell

After it had been established that the generator, when charged with the above electrolyte, would produce elementary fluorine in a satisfactory manner, a series of operating runs were planned for the purpose of determining some of the characteristics of the cell. As nearly as possible, the runs A-1, A-2, and A-3 were made under similar conditions in an effort to obtain reproducible data on the operation of the cell using a carbon anode. Run B-1 was made between runs A-2 and A-3, for the purpose of estimating the efficiency of the cell using a carbon anode. Runs C-1, C-2, and C-3 were made under conditions similar to those under which the A series of runs were made, except that a nickel anode was employed, for the purpose of comparing these two anode materials. Run B-2 was then made to obtain a comparison of cell efficiency using a nickel anode. Run D, using the nickel anode, was made to ascertain the voltage distribution in the cell. Two runs, E-1 and E-2, were made to determine the effect of electrolyte temperature on operating voltages.

Figure 6 shows the arrangement of apparatus that was

employed in the operation of the fluorine generator. The electrolytic cell (B) was placed on a small platform scale as a means of maintaining the electrolyte composition within fairly narrow limits. Hydrogen fluoride was consumed during the electrolysis, with a resultant decrease in the weight of the electrolyte. As the weight of the electrolytic unit decreased due to decomposition of the hydrofluoric acid, more anhydrous hydrofluoric acid could be added from the cylinder through the hydrogen fluoride delivery tube. The hydrogen fluoride delivery tube was connected by means of a length of ¼ inch copper tubing (containing three 10 inch diameter turns, to provide flexibility), a Crane #222 x ¼" - 3000 lb. Exelloy needle valve, a length of cold drawn seamless stainless steel ¼" tubing, and a special kerotest cylinder valve. All connections to tubing were made by means of brass compression joints. A vacuum break was provided in the hydrogen fluoride line to prevent any possible suck-back of electrolyte into the hydrogen fluoride line and consequent plugging of the line.

Two means were employed to obtain the requisite direct current to conduct the electrolysis. A G. E. Tungar rectifier, drawing current from a 110 V. A. C. line, was used in preparation of the electrolyte but was unable to provide the higher currents desired for fluorine generation. The means which received the greatest use was a large lamp bank which drew current from the 220 V. D. C. main.

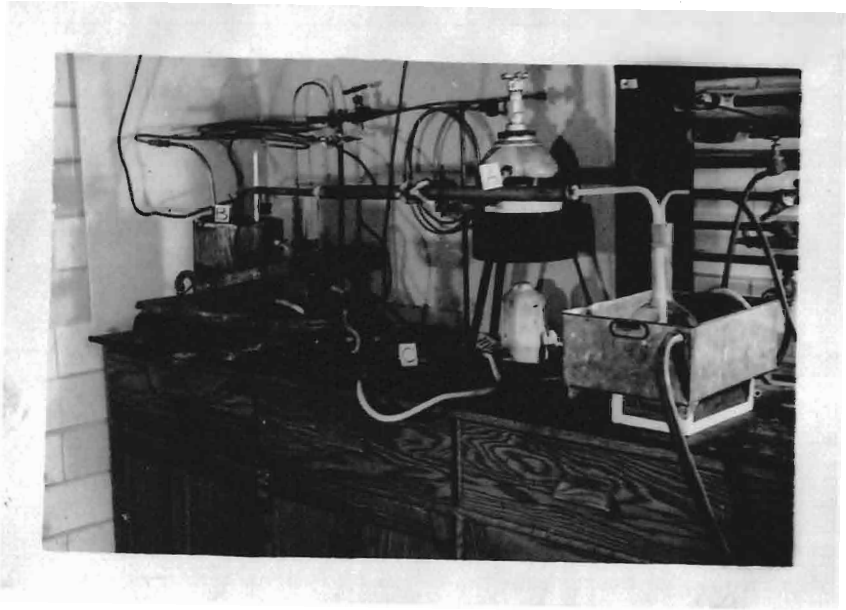

Figure 6. THE FLUORINE GENERATOR IN OPERATION.

The cylinder of anhydrous hydrofluoric acid (center background) is connected to the hydrogen fluoride delivery tube entering the electrolytic cell (B) from the left. The thermometer extending from the cell measures electrolyte temperature. The fluorine outlet from the cell connects to a purification tube (A) for the purpose of removing hydrogen fluoride. At C are the electrical instruments for measuring the cell current and voltages. Operating current was supplied from the 220 V. D. C. power line through a lamp bank suspended overhead, not shown in this picture.

The measuring instruments employed were a Jewell Voltammeter of 150 V. and 30 A. capacity, to measure amperage, over-all voltage, and cathode voltage. A Weston D. C. voltmeter of 30 V. capacity was used to measure anode potential.

The fluorine outlet tube was connected by means of compression fittings to a copper purification tube made of one inch copper tubing and containing sodium fluoride which had been dried for twenty-four hours at 110° C. The purpose of this tube was to remove the hydrogen fluoride from the fluorine as generated(39).

The fluorine leaving the purification tube passed through glass tubing (connected to the purification tube by means of a rubber stopper covered with copper foil) to a flask of carbon tetrachloride, where the fluorine delivery tube dipped just below the surface of the carbon tetrachloride. The gas then left the flask by means of glass tubing to be vented either to the exhaust blower or directly to the outside atmosphere. The flask of carbon tetrachloride was placed in a water bath to maintain a cool temperature. During fluorination processes, the flask of carbon tetrachloride was replaced by the fluorination apparatus.

It was determined whether fluorine was being generated at any time by the use of illuminating gas. A small jet of the hydrocarbon gas was brought into the vicinity of the fluorine delivery tube and if fluorine was issuing from the tube, the illuminating gas burst spontaneously into flame.

Helium was used to sweep air out of the system prior to electrolysis, and as a diluent during fluorination. The

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(39) Wheatly, op. cit., p. 6.

helium was introduced through a nipple on the purification tube at A, figure 6.

Before each run the generator was thoroughly flushed with a stream of helium. If the generator had previously remained inactive for more than three hours, it was allowed to operate at 10 amperes for fifteen minutes to an hour, depending upon the length of time it had remained inoperative, to remove any water that might have been absorbed from the atmosphere by the electrolyte.

An attempt was made to duplicate all conditions for the three "A" series runs, in order to check reproducibility of data. Each run was started at a low current density, and the current was gradually increased by small increments at two minute intervals. Operating data were recorded after each increase of current density. The electrolyte temperature was maintained within as narrow limits as practicable by adjusting the amount of steam or water in the heating jacket. In addition to the over-all voltage, the potential from the anode to the diaphragm (anode voltage) was recorded in run A-3. All data recorded in the three runs of series "A" are listed in Table II. Between runs, the cell was disassembled and examined for corrosion. The carbon anode showed the greatest effect of corrosion, although some corrosion of the copper diaphragm was noted, particularly on the bottom cover plate.

When corrosion of the carbon anode was noted, and be-

TABLE II. FLUORINE CELL OPERATING CHARACTERISTICS USING A CARBON ANODE

Elapsed Time, Min.	Run No.	Amperes	Over-all Voltage	Anode Voltage	Temperature
0	A-1	1.0	6.0		75° C.
	A-2	1.0	7.3		72
	A-3	1.0	7.5	5.2	72
2	A-1	1.5	8.0		79
	A-2	1.5	8.2		77
	A-3	1.5	9.3	5.9	75
4	A-1	2.8	12.3		76
	A-2	2.8	12.0		77
	A-3	2.7	11.6	6.2	77
6	A-1	3.7	14.4		71
	A-2	3.9	13.9		75
	A-3	3.8	14.0	6.3	74
8	A-1	4.5	14.9		73
	A-2	4.6	15.0		73
	A-3	4.5	15.4	6.5	72
10	A-1	5.5	17.5		76
	A-2	5.5	17.1		76
	A-3	5.6	16.1	6.6	76
12	A-1	6.3	18.1		74
	A-2	6.4	19.0		74
	A-3	6.4	18.0	6.7	74
14	A-1	7.5	20.1		71
	A-2	7.4	19.3		72
	A-3	7.5	20.2	6.7	71
16	A-1	9.2	21.2		73
	A-2	9.3	20.9		74
	A-3	9.2	20.3	6.9	74
18	A-1	10.4	22.2		72
	A-2	10.4	21.8		72
	A-3	10.3	21.4	7.0	75
20	A-1	12.0	24.0		71
	A-2	12.0	23.0		72
	A-3	11.9	22.7	7.1	75
22	A-1	13.0	23.0		73
	A-2	13.1	23.5		72
	A-3	13.1	23.3	7.3	74

TABLE II (continued). FLUORINE CELL OPERATING CHARACTERISTICS USING A CARBON ANODE

Elapsed Time.Min.	Run No.	Amperes	Over-all Voltage	Anode Voltage	Temperature
24	A-1	14.2	24.1		74° C.
	A-2	14.2	24.2		73
	A-3	14.2	24.0	7.2	74
26	A-1	15.3	27.3		75
	A-2	15.3	35.0		76
	A-3	14.3	29.0	7.4	73
28	A-1	15.3	55.0		74
	A-2	16.6	50.0		80
	A-3	----	32.0	10.1	76
30	A-1	----	59.0		76

TABLE III. FLUORINE CELL OPERATING CHARACTERISTICS USING A NICKEL ANODE

Time of run.Min.	Run No.	Amperes	Over-all Voltage	Anode Voltage	Temperature
0	C-1	1.5	4.9		72° C.
	C-2	1.5	3.1		73
	C-3	1.5	2.4	2.0	75
2	C-1	2.8	7.5		74
	C-2	2.9	7.7		76
	C-3	2.8	7.2	4.3	79
4	C-1	4.5	11.0		77
	C-2	4.4	10.8		77
	C-3	4.5	11.1	6.0	76
6	C-1	6.6	13.6		75
	C-2	6.5	14.0		74
	C-3	6.4	13.7	6.1	72
8	C-1	8.4	16.0		74
	C-2	8.5	15.8		72
	C-3	8.4	16.7	6.3	73
10	C-1	10.4	18.7		76
	C-2	10.4	18.6		75
	C-3	10.4	19.2	6.2	75

TABLE III (continued). FLUORINE CELL OPERATING CHARACTERISTICS USING A NICKEL ANODE

Time of run. Min.	Run No.	Amperes	Over-all Voltage	Anode Voltage	Temperature
12	C-1	12.0	20.5		74° C.
	C-2	12.0	20.7		74
	C-3	11.9	20.8	6.4	74
14	C-1	13.0	22.0		73
	C-2	13.1	21.9		74
	C-3	13.1	21.1	6.5	72
16	C-1	14.2	22.0		74
	C-2	14.1	22.2		74
	C-3	14.2	21.9	6.6	75
18	C-1	15.3	23.0		76
	C-2	15.3	22.9		73
	C-3	15.2	23.0	6.6	73
20	C-1	16.7	23.5		74
	C-2	16.7	24.2		74
	C-3	16.7	24.1	6.7	73
22	C-1	17.7	23.8		73
	C-2	17.8	24.0		74
	C-3	17.7	23.9	6.9	75
24	C-1	18.9	23.8		74
	C-2	18.9	23.9		75
	C-3	18.9	23.9	6.7	76
26	C-1	19.8	24.1		74
	C-2	19.7	33.2		75
	C-3	19.8	24.1	6.8	75
28	C-1	20.0	24.1		75
	C-2	----	45.0		77
	C-3	20.0	24.3	6.8	74
30	C-1	20.0	24.3		75
	C-2	----	----		--
	C-3	19.9	24.5	6.9	75

fore any further "A" runs were made, it was decided to determine the efficiency of the cell using a carbon anode, for the purpose of comparison with the efficiency using a nickel anode. Consequently, run B-1, to determine the approximate rate of evolution of fluorine from the cell using the carbon anode, was made immediately following run A-2. The data from this run are recorded in Table VI, and a discussion of the method employed will appear in this thesis along with a description of run B-2.

Following the completion of the "A" series, the carbon anode, which was seriously corroded, was replaced by an anode of the same dimensions, constructed of sheet nickel in the form of an open hollow cylinder. The nickel anode was used for the "C" series, which were carried out in the same manner as the "A" series. The data from the three "C" runs are given in Table III.

One run, C', was made to compare the effect of having the cathode separate from the cell body, to allow greater freedom of circulation of the electrolyte around the cathode. An insulated cathode also had the advantage that no hydrogen was generated on the surface of the cell floor; further, the close streamlining of the gases formed at the electrodes obviated the necessity for a diaphragm in the electrolyte.

For run C', two flat strips, 1½ inches wide were cut from sheet nickel to serve as electrodes. These were suspended in the electrolyte approximately 1½ inches apart

and were insulated from the cell body. The bottom cover was removed from the diaphragm, which then served as a bell to collect the fluorine as it was generated. The lower edge of the diaphragm was inserted far enough into the electrolyte to just cover the top row of slots, but not far enough to completely "hide" the anode from the cathode. This run was made as quickly as possible, recording only current and voltage. The data from run C' are tabulated in Table IV.

Discussion of the Data

These data on the fluorine cell operation are plotted in a graph, figure 7, for the purpose of ready comparison of the operation using either carbon anode, nickel anode, or nickel sheet electrodes insulated from the cell body. It can be seen in figure 7 that the highest voltages were

TABLE IV. FLUORINE CELL OPERATION USING SHEET NICKEL ELECTRODES.

Time of run. Min.	Amperes	Over-all Voltage
0	1.5	2.5
1	2.8	4.4
2	4.5	6.0
3	6.6	7.3
4	8.4	8.8
5	10.4	12.7
6	12.0	12.9
7	13.0	13.2
8	14.2	13.9
9	15.3	14.4
10	16.7	14.8
11	17.7	16.5
12	18.9	16.5
13	19.8	16.7
14	20.0	16.8

required using the carbon anode, while the lowest voltages were required with the insulated electrodes. The two upper curves, regarding the carbon and nickel anodes respectively are plots of points which are the average values of the three runs made in each case. It appears from a study of the carbon anode data in Table II that the severe corrosion of the anode had no appreciable effect on the operating characteristics of the cell, since there is good correlation between the three runs regardless of the condition of the anode.

Figure 8 shows the corrosion of the carbon anode (on the left) as compared to the nickel anode. The nickel anode appeared to have been slightly attached at the electrolyte-gas interface, as evidenced by some discoloration of the nickel.

The data of Tables II and III indicate the effect of polarization at high current densities, as evidenced by the sudden increase in voltage. This is demonstrated in figure 7 by a dashed line. Polarization was less frequent when the nickel anode was used, and then occurred only at the highest current densities.

During runs A-3 and C-3 it was observed that the voltage from the anode to the diaphragm increased only slightly after it reached a certain value, while the overall voltage continued to rise with increasing current. Run D was next made to further investigate the voltage charac-

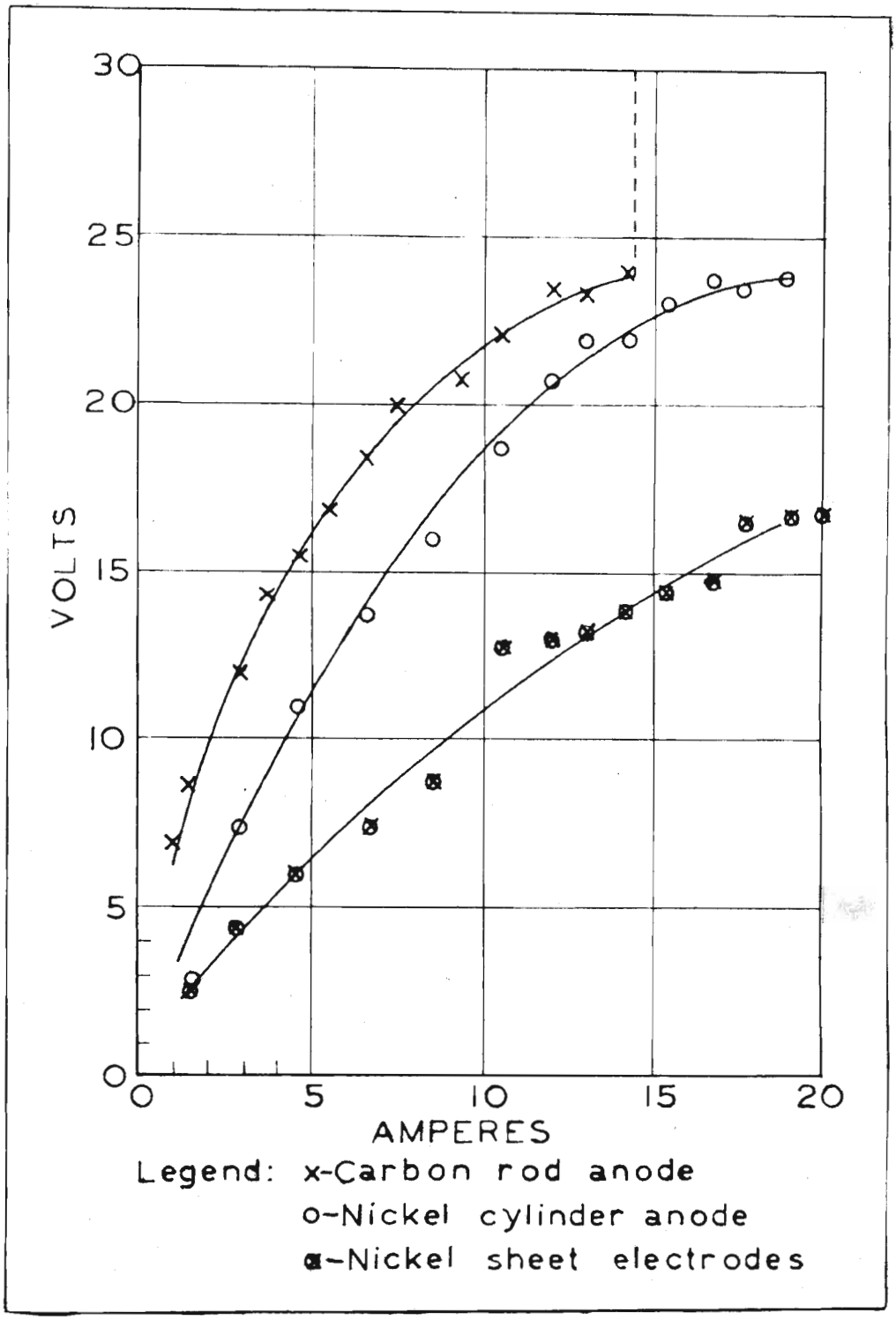

Figure 7. CURRENT-VOLTAGE DATA OF THE ELECTROLYTIC CELL

The upper two curves represent average data of three runs for each curve; the lower curve is a plot of data from only one run.

teristics of the fluorine cell. The same technique was employed for run D as for runs A and C. The electrolyte temperature was maintained at 75° C. plus or minus 4° C. In addition to the over-all voltage, the voltage from the

Figure 8. CORROSION OF THE ANODES

anode to the diaphragm and from the diaphragm to the cathode were recorded. These data are given in Table V and plotted in Figure 9.

Run B-2 was next made to obtain data for comparison of efficiencies with the cell using a carbon anode. No attempt was made to measure accurately the volume of fluorine generated by the cell. Using anhydrous electrolyte with a nickel anode, it was expected that the fluorine formed would be of a high degree of purity, except for the hydrogen fluoride which may have accompanied it from the cell. The hydrogen fluoride was to be removed in the purification tube.

A method was devised for estimating the yield of fluorine which, although far from accurate, was satisfactory to

TABLE V. VOLTAGE CHARACTERISTICS OF A NICKEL ANODE CELL.

Time of run, Min.	Amperes	Over-all Voltage	Anode Voltage	Cathode Voltage
0	1.5	5.2	4.2	1.8
2	2.8	8.1	5.7	2.7
4	4.5	10.3	5.9	3.0
6	6.6	15.1	6.2	4.0
8	7.4	17.2	6.3	5.1
10	8.5	18.4	6.3	5.7
12	10.2	18.3	6.4	6.0
14	12.0	20.6	6.6	6.3
16	12.9	21.4	6.5	6.3
18	14.0	24.0	6.6	6.1
20	15.1	24.0	6.6	6.2
22	17.0	24.2	6.5	6.3
24	18.2	24.4	6.6	---
26	19.2	23.9	6.5	6.2
28	20.1	24.1	6.6	---
30	20.0	24.0	6.5	6.3
36	20.0	34.2	10.1	6.5

TABLE VI. CELL EFFICIENCIES FOR CARBON AND NICKEL ANODES

Run No.	Anode M't'l	Current, Amperes	Bubbles per 12 seconds	Actual Yield, ml/hr	Theor. Yield, ml/hr	Per cent Efficiency
B-1	C	1.5	3	300	627	47.8
B-1	C	2.9	6	600	1210	49.6
B-1	C	4.0	9	900	1670	53.9
B-1	C	6.2	13.3	1330	2590	51.4
B-1	C	8.5	18.3	1830	3550	51.6
B-2	Ni	1.5	3	300	627	47.8
B-2	Ni	2.9	7	700	1210	57.9
B-3	Ni	4.0	10	1000	1670	59.9
B-4	Ni	6.2	16	1600	2590	61.7
B-5	Ni	8.5	22	2200	3550	62.0

give a comparison of the operation of the two anodes. The fluorine delivery tube from the purification unit dipped

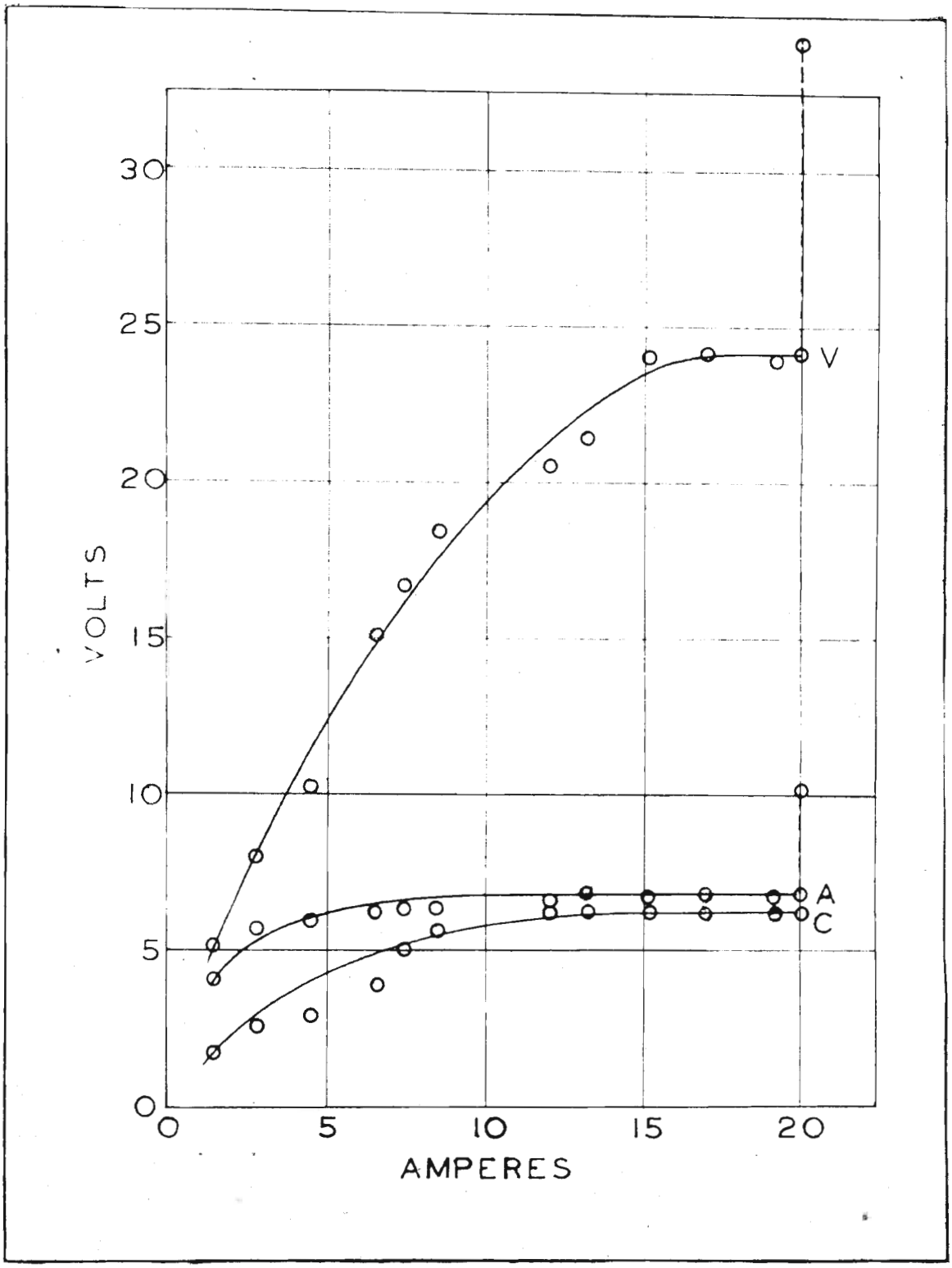

Figure 9. VOLTAGE CHARACTERISTICS OF A NICKEL ANODE CELL

Curve A is the voltage from the anode to the diaphragm, Curve B is the voltage from the diaphragm to the cathode, and Curve V is the over-all voltage of the cell.

just below the surface of the carbon tetrachloride so that the rate at which the bubbles of fluorine formed could be observed. This delivery tube was first calibrated using helium to displace carbon tetrachloride in an inverted graduate. It was found that the number of bubbles counted in twelve seconds multiplied by 100 represented the milliliters of gas evolved per hour. The fluorine molecule was assumed to be diatomic in calculating the theoretical volume based on Faraday's law. The data and calculation of efficiency are given in Table VI. Temperatures were the same for each of runs E-1 and E-2. After each increase of current, sufficient time was allowed to insure practically constant flow, and three bubble counts were taken. Table VI lists the average bubble counts.

Two runs, E-1 and E-2, each at a constant current value of 10.2 amperes were made to ascertain the effect of electrolyte temperature on cell voltage. The temperature of the electrolyte was slowly raised (1 to 2° rise per minute) by increasing the flow of steam in the heating jacket. As predetermined temperatures at approximately 10° intervals were attained, voltage readings were taken. The data so obtained are given in Table VII.

TABLE VII. CHANGE IN VOLTAGE WITH TEMPERATURE.

Run E-1		Run E-2	
Temp.	Voltage	Temp.	Voltage
73° C.	18.7	73° C.	18.8
82	18.2	82	18.5
91	17.8	91	18.0
101	17.5	100.5	17.5

Anode polarization in fluorine generators has been a frequent phenomenon[40],[41], but the cause is not clear. In every run where the current was increased to 20 amperes, except C-1 and C', a point was reached where the over-all voltage suddenly rose sharply due to a high anodic overvoltage. This was quite possibly due to the formation of a film of gas which sheathed the anode and could be pierced only by a high electromotive force. The condition was relieved by momentarily breaking the circuit. This polarization effect was found to be more troublesome with the carbon anodes than with the nickel anodes. It has been recently found[42] that the addition of 1.0 to 1.5 per cent lithium fluoride largely overcomes the polarization.

Operation of the fluorine generator was at times accompanied by small explosions of varying intensity. These appeared to be due to one of three causes: (1) Any restriction or resistance to the flow of fluorine would at times result in some fluorine passing through the diaphragm into the cathode compartment where it would unite explosively with the hydrogen. Such explosions were of mild intensity and relatively harmless. (2) Any moisture in the atmosphere of the anode compartment would at times react explo-

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(40) Cady, Rogers, and Carlson, op. cit., p. 7.

(41) Bigelow, L. A., Chem. Rev., Vol. 40, p. 51 (1947).

(42) Pinkston, J. T., op. cit., p. 9.

sively with the fluorine to form hydrogen fluoride and oxides of fluorine. Similar explosions would also occur if hydrogen happened to get into the anode compartment. The anode compartment explosions constituted a minor hazard in that they were occasionally of sufficient intensity to force part of the molten electrolyte out of the cell. (3) Due to the highly reactive nature of the fluorine, there is the possibility of explosive reactions with various substances. On one occasion, in an effort to eliminate the small explosions in the cathode compartment, a slight suction was applied to the outlet of the carbon tetrachloride flask in order to relieve the back pressure in the fluorine line. There was a violent explosion in the carbon tetrachloride flask. At the time it was believed that hydrogen had been drawn from the cathode compartment through the fluorine line and mixed in explosive proportions with the fluorine. It was later learned that under certain conditions[43] fluorine explodes violently with carbon tetrachloride vapors. However, Whearty[44] reported using carbon tetrachloride in much the same manner as described herein, for a considerable period of time, apparently without danger.

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(43) Bigelow, L. A., op. cit., p. 44.
(44) Whearty, J. F., op. cit., p. 6.

FLUORINATION BY MEANS OF METAL CARRIERS

(Reagents)

The fluorinating agents, cobalt trifluoride, manganese trifluoride, silver difluoride, argentous fluoride, and mercuric fluoride were all obtained as experimental samples from the Harshaw Chemical Company.

The phenol (Mallinckrodt analytical reagent) was considered to be pure enough for use as received.

The 2,4-dichlorophenol was prepared in this laboratory. 0.2 Mole of phenol was placed in a tared flask, surrounded by an ice bath, and chlorine gas from a cylinder was run in very slowly until 0.4 moles of chlorine, as determined by weighing at intervals, had been added. The product (2,4-dichlorophenol) was a pale yellow, crystalline solid.

2,4-Dichlorophenoxyacetic acid was prepared in this laboratory. 2,4-Dichlorophenol (0.1 mole) was placed in a 500 cc round-bottom flask and 5 grams of solid NaOH was added together with 50 ml. of distilled water. 0.1 Mole of monochloroacetic acid (Merck) was dissolved in 100 ml of distilled water and neutralized with NaOH. The sodium chloroacetate thus formed was added to the flask containing the 2,4-dichlorophenol and the flask containing the reaction mixture was placed on the steam cone, at approximately 100°.

After heating on the steam cone for two hours, the flask and contents were cooled. The mass of white crystals that formed upon cooling were filtered off on the Buchner

funnel and washed twice with small amounts of distilled water. The sodium-2,4-dichlorophenoxyacetate was dissolved in a minimum amount of boiling water and acidified to congo red with 3N hydrochloric acid while still hot. The white crystals that formed upon acidification were filtered off on the Buchner funnel, washed with distilled water and recrystallized from boiling distilled water.

A second recrystallization was made from hot alcohol and the purified crystals were dried for four hours in the oven at 110°. This product, 2,4-dichlorophenoxyacetic acid, was obtained in a 53 per cent yield and melted at 137.1°.

The carbon tetrachloride (Mallinckrodt purified) was considered to be satisfactory for use as received. The fluorine used was generated as required.

(Experimental Procedures)

1. Direct Fluorination of Phenol and 2,4-Dichlorophenol

In order to determine the reactivity of the reagents employed, a preliminary direct fluorination was attempted. Solutions containing one gram of phenol in 100 ml. of carbon tetrachloride and 1.5 grams of 2,4-dichlorophenol also in 100 ml. of carbon tetrachloride were prepared. These solutions were placed in side-arm distilling flasks fitted with condensers and were subjected to the following treatment: The fluorine delivery tube was introduced through the top of the flask and extended just below the surface of the solution. The flasks were surrounded with a water bath maintained at about 18°. Fluorine was passed into the flasks containing the solutions at a rate of about 900 cc per hour, using a current of 4.0 amperes, for half an hour.

Results: (1) The phenol solution grew progressively darker in color during the fluorination. Subsequent distillation removed the carbon tetrachloride, leaving a dark, reddish-brown oil of indefinite boiling point and a little dark brown tarry substance. (2) The dichlorophenol solution showed no indication of reaction for the first few minutes, then there was a small explosion of insufficient intensity to break the flask. The reaction was stopped at this point. Subsequent distillation yielded some of the unreacted dichlorophenol and some black tarry substance. No odor was detected above that of phenol.

2. Indirect Fluorination of 2,4-Dichlorophenoxyacetic Acid

Five samples were weighed out, 10 per cent excess of fluorinating agent added, and the reaction mixtures were placed in test tubes:

Sample 2a (CoF_3): 1.11 grams of 2,4-D
1.23 grams of CoF_3

Sample 2b (AgF_2): 1.08 grams of 2,4-D
1.75 grams of AgF_2

Sample 2c (AgF) : 0.93 grams of 2,4-D
1.16 grams of AgF

Sample 2d (HgF_2): 0.89 grams of 2,4-D
1.94 grams of HgF_2

Sample 2e (MnF_3): 0.97 grams of 2,4-D
1.66 grams of MnF_3

The five tubes containing the above dry mixtures were suspended in a bath of cottonseed oil, provided with a mechanical stirrer and thermometer. Each reaction tube was fitted with a long condenser of glass tubing.

The temperature of the oil bath was slowly raised to 190° C. over a period of one hour and forty-five minutes. The temperature was held at 190 - 200° for one hour, then allowed to cool slowly to room temperature.

Results:

Sample 2a (CoF_3): When the temperature reached approximately 140°, the reaction mixture began to darken and a white solid appeared in the condenser. When the reaction tube was opened at the end of the experiment, a strongodor of chlorine was detected. A dark brown crystalline solid was extracted from the reaction mass with ether and gave a melting point of 86 - 89° C.

Sample 2b (AgF_2): During the heating process, at 78°, there

was a sudden reaction which resulted in the formation of dense white fumes, some of which escaped out of the end of the condenser. The reaction mixture began to darken. As the heating continued, no further evolution of fumes was observed, but the reaction mixture grew progressively darker. At the completion of the experiment a strong odor of chlorine was detected. The nature of the black, semi-crystalline residue resulting from this reaction indicated appreciable contamination from side-reaction products, and the sample was not further studied.

Sample 2c (AgF) : The reaction between AgF and the 2,4-dichlorophenoxyacetic acid appeared to require the highest temperature of the reactions investigated. Although it proceeded at a slower rate, it appeared to be at least as complete as any of the other reactions. When the reaction tube was opened at the end of the reaction period, the odor seemed to be predominantly hydrogen chloride. The ether-extracted portion was light orange-brown and consisted of both solid and liquid phases, which did not entirely liquify until a temperature of 85° C. was reached.

Sample 2d (HgF_2): No reaction was noted with this sample until a temperature of 185° was reached, when the color of the reaction mixture began to change slowly from orange (due to the HgF_2) to light gray. At the end of the reaction period, there was a distinct odor of either hydrogen chloride or hydrogen fluoride. The main product was a buff-colored mass that became liquid at about 110° but not at any

clearly defined melting point.

Sample 2e (MnF_3): The action of manganese trifluoride seemed to be the same as that of cobalt trifluoride, and the products of the reaction had the same characteristics.

3. Indirect Fluorination of 2,4-Dichlorophenol

Fifteen grams of 2,4-dichlorophenol were placed in a round-bottom flask fitted with a reflux condenser and thermometer. Twenty-five grams of mercuric fluoride were added, and the temperature was held between 45 and 55°for two hours, during which time there was some evidence of a slow reaction. At the end of two hours, the mixture was decanted to separate the mercury salts, and the products were fractionated.

Results: Most of the mixture distilled over at 200 to 210° and appeared to be unreacted 2,4-dichlorophenol. There remained in the flask a few grams of a dark, reddish-black, very viscous unworkable residue.

4. Indirect Fluorination of Phenol

To five grams of phenol, dissolved in 25 ml of carbon tetrachloride, was added 12.5 grams of argentous fluoride. A reaction, though not violent, began at once at room temperature. The reaction mixture was allowed to stand in a closed flask at room temperature for ten hours. The reaction mixture was then decanted from the silver salt and made basic with strong NaOH solution. This solution was filtered through a wet filter paper and separated from the carbon tetrachloride and insoluble silver salt. The filtered solution, supposedly containing

a sodium salt of phenol or fluorophenols was then added to a solution of sodium chloroacetate and the mixture was heated on the steam cone for two hours, but yielded no precipitate upon cooling. Additional heating for another two hours likewise had no effect.

Results: The reaction with the argentous fluoride yielded a dark red liquid. After treatment with NaOH solution, the red color remained in the carbon tetrachloride layer. When the carbon tetrachloride solution was washed to remove some of the silver salt and fractionally distilled, it yielded a small fraction in the 180 - 184° boiling range, apparently phenol, and a dark viscous and unworkable liquid similar to the residue resulting from the treatment of 2,4-dichlorophenol.

CONCLUSIONS

The Fluorine Cell

The data show that this fluorine cell may be operated simply and with consistent results. The medium range electrolyte was found to be relatively simple to prepare, easy to handle, and readily maintained at operating temperature by the steam jacket. Furthermore, it was not difficult to maintain the electrolyte composition within narrow limits.

The voltage characteristics of this cell seem to be consistent with data reported in the literature for cells of this type (45), but this cell falls short in efficiency. Previous workers have reported cell efficiencies in excess of 90 per cent (46), whereas the best efficiency recorded for this cell was 62.0 per cent. It is quite likely that higher efficiencies would have been obtained at higher current densities (below the point of polarization) since the efficiency was seen to rise as the current increased. The nickel anode gave better operation than the carbon anode.

The data on the operation using an insulated cathode (Table IV) although not sufficient to be conclusive, tend to indicate that a cathode separate from the cell body would result in more efficient operation.

The major shortcomings of this cell appear to be the following: (1) low efficiency, (2) not sufficiently

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(45) Schumb, Young, and Radimer, op. cit., p. 9.

(46) Bigelow, L. A., op. cit., p. 44.

sturdy in construction, (3) open to the air, permitting the electrolyte to absorb moisture if it stands inoperative for a considerable period of time, (4) a tendency to small explosions within the cell.

It is believed that the main reason for the low efficiency was contamination of the electrolyte, principally with copper salts. The preparation and maintenance of a reasonably pure electrolyte, plus the precaution of good electrical contacts, should result in much higher cell efficiencies.

Following are some design recommendations based on experience with this cell: (1) Monel metal or stainless steel construction material for the major parts of the cell. (2) Nickel anode; (3) A closed top to keep the electrolyte anhydrous when the cell is not in use; (4) Cathode insulated from the cell body; (5) Anode of solid construction (not an open cylinder which permits electrolyte to get within the anode); (6) Level of electrolyte well above the bottom of the diaphragm to lessen the possibility of fluorine passing into the cathode compartment; (8) Inert gasket and insulating material, such as "Teflon", which was recently made available by E. I. duPont, Inc.

The Fluorination Operations

The work of previous investigators was corroborated by experiment 1, in that it was demonstrated that direct fluorination is difficult to control and results in many side reactions.

The results of experiment 2 tend to indicate the following order in decreasing activity for the fluorinating agents investigated: AgF_2, MnF_3, CoF_3, AgF, HgF_2. Very little difference was displayed between MnF_3 and CoF_3. Argentous fluoride and mercuric fluoride also gave approximately the same results. More data in this regard should be obtained before definite conclusions can be drawn.

The only conclusion that can be made regarding the attempts at synthesis is that the methods or techniques used for effecting the synthesis of a fluorinated phenoxyacetic acid were unsatisfactory, but the results do not justify abandonment of the project. Although the natural course of the reaction would be a direct replacement of chlorine with fluorine, there are many possible side reactions and methods were not found for controlling these.

The synthesis of 2,4-difluorophenoxyacetic acid was approached from three different directions but none of them yielded success: (1) Halogen substitution by fluorine into 2,4-dichlorophenoxyacetic acid by means of metal carriers resulted only in an indefinite mixture of complex substances; (2) Attempts to replace the chlorine of 2,4-dichlorophenol, or, (3) to fluorinate phenol to 2,4-difluorophenol both gave the same negative result: a viscous residue of what was apparently a mixture of polymerized substances.

SUMMARY

1. An electrolytic cell for the generation of fluorine was designed and constructed, embracing the following modifications or improvements: (a) a means of conveniently ascertaining and maintaining the electrolyte composition, (b) a flexible method of controlling the electrolyte temperature, (c) simplicity of construction, (d) a baffle to prevent entrainment of the electrolyte into the fluorine delivery tube.

2. A technique for conveniently preparing an electrolyte of the composition $KF \cdot 2HF$ was devised and employed.

3. The operating characteristics of the cell were investigated by a series of runs. It was determined that the following will provide optimum operation of the cell: (a) electrolyte temperature close to 100° C., (b) current of 12-15 amperes, (c) cell approximately 2/3 full of electrolyte. (d) a nickel anode.

4. Under favorable conditions, the cell was consistently operated at the following values: over-all voltage, 20 - 23 volts; cell efficiency, at least 62 per cent.

5. Recommendations for an improved cell, based upon experiences in operating the present cell were set forth.

6. The relative fluorinating power of the following metal carriers was investigated: CoF_3, MnF_3, AgF_2, AgF,

and HgF_2. It appeared that AgF_2 had the greatest activity, CoF_3 and MnF_3 occupied intermediate positions of about equal strength, and AgF and HgF_2 were the weakest of the fluorinating agents investigated.

7. Repeated attempts under varying conditions to prepare 2,4-difluorophenoxyacetic acid by halogen replacement in 2,4-dichlorophenoxyacetic acid always yielded an indefinite mixture of complex substances.

8. Attempts to prepare 2,4-difluorophenol, (which could be used as an intermediate in the synthesis of 2,4-difluorophenoxyacetic acid) by two different methods invariably yielded only a viscous, unworkable residue.

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VITA

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