THE ACTION OF ELEMENTARY FLUORINE UPON ORGANIC COMPOUNDS

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Received July 17, 1946

CONTENTS

I. INTRODUCTION

The element fluorine was first isolated in 1886 by Henri Moissan, Professor at the École Supérieure de Pharmacie in Paris, working in coöperation with the French Academy of Sciences. His work was characterized throughout by a high degree of scientific precision and was, incidentally, warmly commended by his colleagues (25) of that day. Fluorine is the most electronegative, and probably the most reactive, of all the known elements, so that the technical difficulties and expense involved in preparing the gas were at first very great. As a result, the development of our knowledge of the fundamental properties, reactions, and possible uses of the element and its compounds was correspondingly slow. However, in recent years this advance has been proceeding at a rapidly accelerating rate in many directions,—inorganic, organic, industrial (as in refrigerants and insecticides), and medical (as in the study of dental caries).

In the field of organic chemistry the development has proceeded along two general lines: (*1*) indirect fluorination and (*2*) direct fluorination. The first of these consists essentially in the introduction of the element into organic compounds by means of reagents such as antimony fluorides (Swarts reaction), hydrogen fluoride in the presence of antimony or other metalloid halides as catalysts, fluoboric acid (Schiemann reaction), or in other ways. The replacement of aliphatic or otherwise reactive chlorine by fluorine, using hydrogen fluoride as the reagent, often in the presence of antimony halides as catalysts and frequently under pressure, has a number of important advantages, since the reactants are relatively inexpensive, the changes usually take place smoothly, and all of the fluorine is at least theoretically available. On the other hand, this method cannot in general be used successfully either with aromatic chlorine, or to prepare fluorocarbons or other perfluorinated compounds which are of much significance. These indirect procedures have, quite naturally, undergone important development, but it is not proposed to discuss them here.

The second method consists in the direct reaction of the gaseous element with organic compounds under a variety of conditions. This procedure leads readily to the formation of completely fluorinated organic molecules, as the result of substitution, addition, polymerization, or cleavage, which possess valuable properties and cannot in general be prepared successfully in any other way. The direct method, which is to be dealt with fully in the following pages, has certain obvious disadvantages, all of which are being greatly reduced by recent developments. Elementary fluorine is still relatively costly and its reactions are energetic and must be adequately controlled, while in substitution reactions only half of the fluorine is directly available, although the remainder may easily be recovered as hydrogen fluoride and used again.

The earlier studies dealing with direct fluorination were beset with many difficulties due to the great reactivity of the element, and it was soon found that the gas combined with most carbon compounds essentially by combustion and often explosively, yielding only carbon tetrafluoride, hydrogen fluoride, and free carbon. It required nearly half a century of slow progress before ways and means were found to control and direct these powerful reactions, but now the

importance of the resulting fluorocarbons and their derivatives is increasing rapidly. Incidentally, it is beginning to look as if processes involving a combination of indirect methods with direct fluorination may have great possibilities in the preparation of such materials on a large scale. Great advances have been made along these lines during the war years, but since most of this work has not yet (1945) been published, it cannot, in spite of its interest and importance, be dealt with in these pages. However, it will be abundantly clear from what follows that the fundamental importance of elementary fluorine in its reactions with organic compounds has been firmly established.

Perhaps a short sketch covering the broad outlines of the work done in this field for the purpose of orienting the reader may not be out of place at this point. In general, direct fluorination using the element itself as the reagent can be carried out in four quite different ways, and these, listed in the approximate order of decreasing importance at the present time, are (*1*) in the vapor phase, over a metal screen packing, (*2*) in solution in an inert solvent, (*3*) in the liquid phase, by counter-current flow, and (*4*) in the solid phase, mixed with a solid, inert diluent.

The vapor-phase method, which has undergone considerable development in the writer's laboratory and elsewhere, following an earlier observation by Fredenhagen and Cadenbach, requires only a heated or cooled brass pipe reactor filled with a copper wire or screen packing, which may be silver plated. The sample, a gas or volatile liquid, which may be diluted with or carried in on nitrogen or other inert gas, is introduced into the reactor along with the fluorine, which itself may be diluted, and reacts quietly within the meshes of the packing. The products are withdrawn progressively, separated, and rectified. This method succeeds presumably because the large surface breaks up the reaction chains, and the bulk of metal rapidly conducts much of the large amount of heat produced away from the reaction zone. It is limited only by the volatility of the sample, since it is not effective in the presence of liquids. Also, if the temperature must be raised too high in order to maintain the vapor phase, molecule smashing by the energetic fluorine atoms occurs, and the product is a mixture of polymerized fragments which cannot be separated easily. Even such a mixture, however, may have valuable physical and chemical properties. Methane, ethane, acetone, benzene (to C_6F_{12}, etc.), and numerous other compounds have been successfully fluorinated by this procedure.

Direct fluorination in solution has been studied principally by Bockemüller, who used mostly a cylindrical metal reactor equipped with baffle plates and containing a dilute solution of the sample in carbon tetrachloride. Fluorine, diluted with carbon dioxide, was bubbled directly through the solutions, and in many cases reacted quite smoothly, after which the products were worked up in orthodox fashion. The reaction presumably takes place at the gas–liquid interface in the bubbles, and the procedure is limited by the relative reactivities of the sample and the solvent toward fluorine. The writer has found that such reactions may be accompanied by deep-seated chlorination of the organic molecule, and also by powerful reactions involving the solvent vapor. The butyric

acids, tetrachloroethylene, crotonic acid, oleic acid, and even benzoic acid (by addition, etc.) among others were successfully reacted in this manner. Liquid fluorocarbons cannot be used in this kind of procedure, since organic compounds in general are not sufficiently soluble in them, but Freon (CF_2Cl_2) and liquid hydrogen fluoride have been used successfully as solvents by Bockemüller and Simons, respectively.

Fluorinations in the liquid phase have been the subject of a preliminary but valuable study by Miller, who employed a metal pipe U-shaped reactor either heated or cooled, in which the fluorine bubbled directly through the liquid sample, which was flowing in the opposite direction. Here, too, the reactions presumably took place at the gas–liquid interface in the bubbles, or possibly in the vapor phase. This procedure is thus far limited to compounds which are relatively inert toward fluorine, and which possess vapor pressures and melting points sufficiently low. High vapor pressures result in too powerful reactions occurring in the vapor phase. Tetra- and pentachloroethanes, as well as tri- and tetrachloroethylenes, among other compounds, have been fluorinated successfully by this procedure.

Direct fluorination in the solid phase has not often been successful, although some solid chlorocarbons like hexachlorobenzene or hexachloroethane do not react violently with the gas on contact. Ruff passed a current of fluorine through a cooled mixture of silver cyanide with an inert solid diluent, supported on a porous bed of like material, and condensed the effluent gases. Some very interesting, unusual, and highly stable compounds were isolated from the product, such as CF_3NF_2, $FCONF_2$, and the dimer $(CNF_3)_2$. This method, however, seems at present to be quite restricted in its applicability.

Turning now to the more detailed presentation, it is desirable to make clear at the outset the general plan according to which the material involved is to be organized. In the leading section there will be given a critical, specific, and fairly complete outline of the studies which have been made in the field from the time of Moissan's original discovery in 1886 to the end of 1945, so far as they have been reported in the literature. This material is to be classified chronologically by leading investigators, rather than in the more usual arrangement by methods and topics. It was felt that this would lead to a much more coherent presentation, since the number of independent contributors in this new and difficult field is quite limited, and they have attacked the problem in very different ways, often obtaining complex results involving several kinds of reactions occurring simultaneously. This means that the contributions of each scientist and his collaborators during the period covered by this review will be considered together, presumably in the order of their natural development within the group. In each case, since the material involved is relatively unfamiliar and widely scattered through the literature, it is planned to present a detailed summary of (*1*) the methods employed and (*2*) the results obtained; after which, whenever it seems practicable, the writer will endeavor to offer some appraisal of the results, either singly or collectively, in the light of recent developments and experience.

Following this more or less factual presentation, a tabular summary will be given including practically all of the well-characterized organic fluorine compounds which have been made by direct fluorination, together with the names of the investigators who first prepared them and the leading references. It is hoped that by this means a reader having in mind either a particular person, or a definite compound, will have no difficulty in locating either the discussion presented here or the original papers.

Later on, a special section is to be devoted to postulated reaction mechanisms and other similar considerations. While this theoretical presentation cannot hope to be complete or in any sense final, an endeavor will be made to give the reader some idea of how the reactions involved in direct fluorinations have most frequently been explained.

Following this, there will be given a detailed account of the construction and operation of a selected number of typical fluorine generators, since the gas has almost without exception been generated as used and has not as yet (1945) been made available commercially. A tabular summary covering all such units which have been mentioned in the literature will also be found in this section.

Finally, a description of the quantitative analysis of fluorine gas will be included, since this important and much neglected subject deserves much greater attention than has usually been paid to it.

II. THE ACTION OF ELEMENTARY FLUORINE UPON ORGANIC COMPOUNDS

A. MOISSAN,[1] *Meslans, Chavanne: pioneer work in France*

Quite naturally, Moissan (66) was the first to observe the effects, now so well known, of bringing elementary fluorine into direct contact with various organic substances. In the main, uncontrolled reactions, combustion, or even detonation took place, with the ultimate destruction of the organic molecule and the formation of hydrogen fluoride and fluorocarbons. Meslans (56), a pupil of Moissan's, subsequently described similar results. Moissan also studied the reactions of fluorine with the various forms of carbon and reported (64, 65) the isolation of carbon tetrafluoride by several methods, accompanied by an analysis. However, his careful efforts to purify the mixture originally obtained were actually unsuccessful, since the reported boiling point (−15°C.) bore no relation to that of pure carbon tetrafluoride (b.p. −130°C. (76)). Considerably later, Moissan and Chavanne (68) attempted to react solid methane (m.p. −184°C.) with liquid fluorine at −187°C., but even at this very low temperature the reactivity of the halogen was so great that the only result was a powerful explosion.

B. BANCROFT, Humiston, Jones, Whearty: pioneer work in the United States

On account of the many experimental difficulties involved in the original preparation of fluorine, as well as those resulting from its great chemical reactivity, no further studies dealing with the reactions of the element with organic com-

[1] The name of the leading investigator in each group appears first.

pounds were attempted for nearly thirty years after Moissan's early work was completed. Then a program of research was begun, initiated during the first World War and conducted either under the general supervision of, or in direct collaboration with, the physical chemist W. D. Bancroft. The first results were described in 1920 by Humiston (45), who, using a Mathers generator (see below) and relatively simple equipment, brought fluorine, at times diluted with nitrogen, into direct contact with carbon and a number of simple organic compounds. He found that the carbon burned to a mixture of fluorocarbons and that acetone and paraffin hydrocarbons took fire at once, while phosgene, chloroform, and chlorocarbons were much less reactive, although free chlorine was liberated in each case. No pure products were isolated, and perhaps the most important observation recorded was that when fluorine was passed through a solution of tetrachloroethylene in carbon tetrachloride, the chlorine set free reacted with the solute to produce considerable hexachloroethane. The powerful chlorination reaction set up when fluorine is passed into solutions of organic compounds in carbon tetrachloride has since been amply demonstrated.

Some years later, Bancroft and Jones (4), who were chiefly interested in electrochemical rather than chemical changes, reported that when benzene vapor and fluorine were mixed, there was a short induction period followed by an explosive reaction. They also noted that the fluorination of a solution of aniline hydrobromide resulted in bromination rather than fluorination, and that when aniline hydrofluoride was similarly treated, only tarry products were formed. Subsequently Bancroft and Whearty (5), and also Whearty (91), reduced the extreme reactivity of the fluorine somewhat, either by operating at lower temperatures or in solution, or by using less reactive samples. They collected considerable amounts of fluorine over an apparently little disturbed mercury surface, and then forced the gas, at a controlled rate, either directly through a liquid sample or upwards through a solid under conditions such that a liquid fluorination product might drain away and later be withdrawn from below. They found that compounds such as benzene, toluene, and anisole yielded no definite products under these conditions, and concentrated their efforts on the fluorination of solid hexachlorobenzene and a solution of 1,3,5-trichlorobenzene in carbon tetrachloride. In the first case, they obtained two products, believed to have been the compounds $C_6F_2Cl_4$ and $C_6F_3Cl_3$, respectively; in the second, they isolated one substance, thought to have been the compound $C_6HF_3Cl_2$, and their claims were supported by analytical figures. Unfortunately, however, the validity of these claims is open to question. In the first place, two of the three products boiled over wide ranges, and only one of them yielded numerically satisfactory analyses, a fact which may or may not be significant; but much more important is the admitted fact that the analytical procedure for fluorine did not give acceptable values even when applied to pure fluorobenzene. Finally, in the light of more recent work to be reviewed later, it is very doubtful if either any hydrogen or even any considerable proportion of aromatic structures could have survived the prolonged fluorination under the conditions described. Altogether it must be concluded that in all probability

the products which have been described here were neither chemical individuals, nor did they consist chiefly of the compounds claimed, although the possibility that they may have contained small quantities of one or more of these compounds is not excluded. While it may appear at first glance that these researches did not yield significant results, it should nevertheless be borne in mind that they represent a definite advance into an entirely new and uncharted field, in which the expected analogies did not hold and the usual background of literature, knowledge, and experience did not exist.

C. FICHTER, Humpert, Bladergroen: fluorination compared with electrolytic oxidation

The next investigator to attempt an organic fluorination was Fichter, an inorganic electrochemist, interested in comparing the reactions of fluorine with electrolytic oxidations. In 1926 Fichter and Humpert (31) passed fluorine over solid potassium acetate, a procedure which resulted either in an explosion or a slower total destruction of the molecule, depending upon whether the salt was hydrated or not. Then they conducted the gas into aqueous solutions of potassium acetate, and obtained ethane and carbon dioxide, which would also have been produced at the anode during the electrolysis of the salt in the Kolbe synthesis of hydrocarbons. The obvious similarity was emphasized, and diacetyl peroxide was postulated as the intermediate product in the fluorination. Later, Fichter and Bladergroen (30) passed fluorine through solutions of alkali carbonates, and presented evidence indicating that percarbonates, such as $K_2C_2O_6$, were formed by a similar process. These early observations, which seem to have been made carefully, are of interest in that they shed a little light on what might be expected during the fluorination of a carboxylic acid or similar acidic compounds.

D. LEBEAU, Damiens: isolation of carbon tetrafluoride

Almost simultaneously, Lebeau, another inorganic chemist, entered the field, if but only a little way, through his study of the inert gas sometimes formed along with fluorine at a carbon anode during the electrolysis of fused metal fluorides, and also by the direct fluorination of wood charcoal. In 1926 Lebeau and Damiens (53) collected a quantity of this gas mixture, and from it isolated by repeated fractionation carbon tetrafluoride, with a molecular weight of 87.4 (calculated, 88), based on the density 3.034 at N.T.P. They described a few of the chemical reactions of this inert compound, and placed its boiling point at "close to −150°" (which is incorrect) but gave no analyses. Several years later Ruff (see below) repeated the work and completely characterized the compound carbon tetrafluoride; immediately thereafter Lebeau and Damiens (54) extended their work, and isolated carbon tetrafluoride (m.p. −191°C., b.p. −126°C.), but again offered no analyses. They also claimed the isolation of C_2F_6 and C_3F_8, but gave no details. It seems quite clear that while the skilled French scientists were the first to isolate carbon tetrafluoride, they cannot quite be credited with the most accurate characterization of this important compound.

E. RUFF, Keim, Bretschneider, Luchsinger, Miltschitzky, Giese, Willenberg: fluorination of carbon, graphite, carbon tetrachloride, fluoroform, and silver cyanide

Next in order to take up the study of fluorine in organic chemistry was Otto Ruff, also an inorganic chemist, who had been working with this gas for many years, and had already made important contributions to the knowledge of its reactions with many of the elements and their compounds. In 1930 Ruff and Keim (76) passed a current of fluorine over purified wood charcoal contained in a glass tube. The carbon ignited spontaneously and in time was completely consumed, leaving only a little ash. The gaseous, low-boiling products of the combustion were condensed in receivers cooled by liquid air and protected from moisture, after which the condensate was fractionated repeatedly from a small, electrically heated quartz still completely immersed in liquid air (81). There were obtained a major fraction consisting of carbon tetrafluoride; a smaller, higher-boiling portion, believed on account of its variable molecular weight and chemical inertness to be a mixture of C_2F_6 with C_3F_8; and a relatively inconsiderable residue, boiling above 0°C., whose average molecular weight approached that of C_6F_{12}. Incidentally, when the charcoal was replaced by graphite, which, on account of its molecular structure, might be expected to yield C_6F_{12} on fluorination, a greater proportion of this high-boiling residue was obtained. Also, some carbon dioxide, produced from oxygen contained in the fluorine, and a little silicon tetrafluoride from the glass were present in the mixture. Presumably owing to the relatively low fractionating power of the ingeniously constructed low-temperature still, only the major fraction was completely separated, and yielded pure carbon tetrafluoride (m.p. -186°C. $\pm$ 1°; b.p. -130°C. $\pm$ 1°) by the vapor-pressure method. Adequate analytical figures were presented, and the compound otherwise completely characterized. Metallic sodium, magnesium, and barium ignited when heated with carbon tetrafluoride, but beyond this the gas was shown to be extraordinarily inert toward a great variety of metals and reagents, as well as essentially insoluble in all ordinary solvents.

Several years later, Ruff and Bretschneider (74) continued the study of the fluorination of carbon and made the interesting observation that when either Norite or graphite was exposed to a current of the gas at a temperature somewhat below the ignition point, the carbon absorbed fluorine progressively until the mixture had the approximate composition required by the formula $(CF)_x$. Also, it was found that if the temperature of the mixture was subsequently raised, as by the onset of ignition, the product would decompose, often with explosive violence, into free carbon (soot or graphite), and a mixture of homologous carbon fluorides, possibly including C_6F_{12}. The substance was most readily prepared by conducting a current of fluorine, purified by first passing through a liquid-air trap and then through an electric discharge, for 4 hr. at a pressure of 25 mm. over a sample of carefully prepared Norite in a copper boat contained in a copper tube and maintained at a temperature of 280°C. Under these conditions the ratio of C:F in the product was 1.18:1, as determined by the increase

in weight of the sample. The product was in all cases a grey powder, stable in a vacuum at room temperature, insoluble in ordinary solvents, and wet by organic liquids but not by water. It did not react with hydriodic acid, aqueous acids or bases, or even hydrogen at 400°C., but was decomposed by heat, metallic sodium, oxidizing alkali fusions, and slowly by zinc dust and acetic acid. It was considered to be a true chemical individual on account of its characteristic grey color, constancy of composition, ionic lattice structure, very low conductivity compared to that of graphite, and because it could be prepared by the action of widely varying concentrations of fluorine on both Norite and graphite, which themselves possess such widely different molecular structures. For analysis the compound was decomposed by heating to 800–900°C. for 10 min. with metallic sodium in a small iron tube welded shut at both ends, followed by determination of the fluoride ion as PbClF. The results indicated that the ratio of C:F in the compound was 1.085:1, which gave a considerable measure of support to the claim that it could best be represented by the formula $(CF)_x$. Further support was also obtained from x-ray data, which, together with the postulated mechanism of the reaction, will be discussed in Section III. Altogether, the claim that a compound of the composition $(CF)_x$ actually exists seems quite well confirmed by the accumulated mass of evidence just described, and this evidence will become practically conclusive when the experimental work involved has been repeated and checked by others.

While these studies dealing with the fluorination of carbon were in progress, Ruff and Keim (77) attempted to fluorinate carbon tetrachloride by passing fluorine through it, but found that while at room temperature little reaction occurred, at reflux temperatures dangerous explosions took place frequently, caused perhaps by the presence of chlorine fluoride in the gas. They sought to avoid this by introducing a volatile catalyst, such as iodine, arsenic, or tungsten. Since these substances react with fluorine in different valence states, they might be expected to act as intermediate fluorinating agents, or buffer substances, and so moderate the intensity of the reaction. It was found that when fluorine was introduced into the vapor of boiling carbon tetrachloride containing iodine, the mixture ignited at the tip of the delivery tube, in the presence of traces of the solid catalyst, and thereafter the fluorine burned continuously and safely in the halide vapor, with the production of a mixture of all the expected products. Afterwards, it was found even better to carry out the reaction in a slightly heated copper tube over a solid cobaltic fluoride (CoF_3) catalyst, the apparatus being so arranged that a current of carbon tetrachloride vapor, carried in on nitrogen, was mixed with the fluorine as it passed over the forward end of the catalyst layer. The products of the smooth, quiet reaction were washed with alkali, condensed, and finally fractionated repeatedly. When the molar ratio of CCl_4:F was 1:1, for example, the compounds $CFCl_3$, CF_2Cl_2, CF_3Cl, and CF_4 were formed to the extent of 32, 47, 16, and 5 mole per cent, respectively, but these proportions varied widely with the experimental conditions, as might be expected. Each of the fluorochlorides was highly purified and its physical constants reported, including analyses of the last two only, since the trichloride had

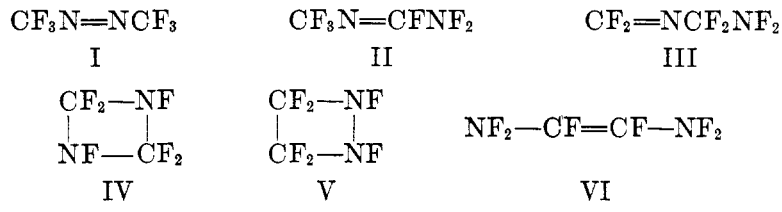
already been characterized by Swarts (90), who made it by an indirect method. The compounds listed above melted at −111°C., −160°C. ± 1°, −181°C. ± 2°, −186°C. ± 1° and boiled at +24.1°C., −28°C., −80°C., and −130°C. (vapor-pressure method), respectively. The reactivities of these halides with a large number of substances were studied, and were found to increase progressively with the chlorine content.

This relatively simple and convenient process of direct fluorination over a metal halide catalyst, seemingly but little noticed at the time, actually gave real promise of significant development, as has been well demonstrated in later years. It may perhaps also be noted at this point that somewhat later in the middle of a paper describing the indirect fluorination of iodoform Ruff, Bretschneider, Luchsinger, and Miltschitzky (75) observed that the direct combination of fluorine with fluoroform (CHF_3) led to ignition and the formation of not only carbon tetrafluoride but also hexafluoroethane. This represents perhaps the first instance of the building up of a carbon chain by direct vapor-phase fluorination, a phenomenon which has since become of increasing importance.

Following the studies dealing with elementary carbon, Ruff and Giese (78) fluorinated silver cyanide, and finally obtained a most interesting and extraordinarily complex reaction product. The solid sample, mixed with solid calcium fluoride to prevent violent explosions, was placed on top of a layer of pure fluorspar contained in a vertical flanged copper cylinder, maintained at 0°C. and equipped with a tight lid carrying the requisite exit tube for the products. The fluorine was led in through a copper side tube, so arranged as to deliver the gas into the underlying fluorspar layer, while the exit gases were condensed in quartz traps by liquid air and subsequently fractionated with great care. In this way there were obtained, along with carbon tetrafluoride, silicon tetrafluoride, carbonyl fluoride, carbon dioxide, nitrous oxide, nitric oxide, and polymerized residue as by-products, essentially three main fractions. The first was a colorless mixture (m.p. about −130°C., b.p. about −78°C.), about 28 per cent by volume; the second, a colorless eutectic (m.p. −128°C., b.p. −40°C.) with a composition and molecular weight corresponding to the formula $(CNF_3)_2$, about 60 per cent by volume; and the third, a dark blue substance (m.p. about −150°C., b.p. about −80°C.) with constants corresponding to the formula CF_3NO, about 2 per cent by volume. It was shown that the oxygen in this last compound came most probably from silver nitrate in the original cyanide. The first mixture could be resolved neither by fractionation nor by any ordinary chemical means, since it was completely inert toward all kinds of laboratory reagents except heated sodium. However, when this material was fluorinated at red heat, it yielded pure carbon tetrafluoride and nitrogen trifluoride in approximately equal proportions, together with pure hexafluoroethane; on this basis it was concluded that the original mixture consisted solely of the compounds CF_3NF_2 and C_2F_6.

In a subsequent paper Ruff and Giese (79) studied very carefully the second and also the main fluorination product of silver cyanide, referred to above as a eutectic (m.p. −128°C., b.p. −40°C.) having the exact composition corre-

sponding to the formula $(CNF_3)_2$. This material was presumably formed by the dimerization of $FN{=}CF_2$, which, in turn, might be expected to result from the action of fluorine on $AgN{=}C$, and was recognized as a mixture of isomers since it would react in part, but not completely, with certain reagents. It may have six possible structures, as follows:



of which I, II, and VI can exist in *cis* and *trans* forms. First a sample of the gas was treated with liquid ammonia in a sealed tube, which caused the appearance of fluoroform and nitrogen in the gas phase, presumably owing to the ammonolysis of II; and also of more fluorine in the residue than could be accounted for in this way, a result which was attributed to the simultaneous destruction of III and V by the reagent. The unchanged gas which had survived this treatment was then shaken with metallic mercury, resulting in the very slow appearance in the gas phase of a compound containing two fluorine atoms per mole less than the original, which was considered due to the reaction of the mercury with IV. After this, a new sample was treated first with mercury, which caused a two-stage reaction, fast at the outset and then slow, which was thought to be due to the successive attack of the metal on V and then on IV. Finally, the surviving gas was treated with liquid ammonia, with the formation of fluoroform and nitrogen as before. These results were well supported by exhaustive analyses, and it was postulated that the ammonia reacted with carbon–nitrogen double bonds, while the mercury attacked the $\rangle NF$ linkage exclusively. Ultimately it was concluded that the original mixture contained at least five of the six possible isomers; by means of a complex calculation frankly described as "more or less" convincing, it was estimated that isomers I, II, III, and IV (or V) were present in the mixture to the extent of about 52, 15, 26, and 8 per cent, respectively.

It should be noted here that considerably later on Ruff and Willenberg (82) reported the synthesis of $CF_3N{=}NCF_3$ (I) by the action of iodine pentafluoride on iodine cyanide, and characterized it as a slightly greenish, very inert gas (m.p. −133°C., b.p. −31.6°C.). Some $(CF_3)_2NH$ (m.p. −130°C., b.p. −6.2°C.) was also formed in this reaction.

In a final article of this series, Ruff and Giese (80) carried out an exhaustive study of the third portion, described above as a blue compound (m.p. about −150°C., b.p. about −80°C.) having the exact composition corresponding to the formula CF_3NO. This material, after very careful purification, was finally found to melt at −196°C. (freezing-point curve), and to boil at −84°C. (vapor-pressure curve). The very low melting point, together with the wide liquid

range, gave rise to the suspicion that this portion, too, might be a mixture of the two possible isomers CF_3NO (blue) and $FCONF_2$ (colorless), and it was therefore treated with a wide variety of reagents in order to effect a separation if possible. It was found that zinc dust and acetic acid, platinum sponge and hydrogen, and manganese heptoxide in acetic acid each destroyed approximately half the sample, leaving the colorless isomer $FCONF_2$, while dilute sodium hydroxide and adsorption on charcoal completely rearranged the blue compound into the same colorless isomer, without change of volume or molecular weight. The completely pure $FCONF_2$ melted at -152.5°C., boiled at -82.4°C., and was so extraordinarily stable that it would react neither with any ordinary reagent tried, nor even with elementary fluorine itself at red heat, but only with the heated metallic sodium used in the analysis. It was recognized that such a compound, when regarded as a derivative of carbonyl fluoride, would certainly not be expected to possess any such stability, especially toward hydrolysis, but no further explanation of the phenomenon was given. From the corresponding vapor-pressure curves, it appeared likely that the boiling point of pure CF_3NO should be very close to that observed for the blue mixture, or -84°C., but the melting point should be much higher, and probably close to -150°C.

Summing up the results of these last three papers, it appears that Ruff and Giese have convincingly demonstrated the formation of the new and interesting compounds CF_3NF_2, $(CNF_3)_2$ (several isomers), and $FCONF_2$ by the direct fluorination of silver cyanide, and have given a considerable description of the physical and chemical properties of these substances. However, only one of them, $FCONF_2$, could be obtained entirely pure and free from other molecular species.

It remains to be said here that the extensive work of Ruff and his collaborators, of which the above sketch dealing with carbon compounds represents but a small fraction, is in general characterized by a measure of insight, experimental skill, and painstaking care which confer upon it a high degree of scientific trustworthiness.

F. ISHIKAWA, Murooka

The next year after Ruff began to study the fluorination of carbon and its compounds, Ishikawa and Murooka (46) reported the approximate fluorine concentrations, varying from 8–16 per cent, presumably in air, required to ignite a number of common organic liquids. They did no further work with elementary fluorine, but later on became interested in oxygen fluoride.

G. BOCKEMÜLLER: fluorination of n- and isobutyric acids, cyclohexane, n-hexadecane, tetrachloroethylene, crotonic acid, oleic acid, and benzoic acid (all in solution)

It was in 1933 that the organic chemist Wilhelm Bockemüller (10), after a considerable experience with indirect fluorination using lead tetrafluoride (29) and phenyl iodide fluoride ($C_6H_5IF_2$) (9) as reagents, published the results of an intensive study of the direct fluorination of organic compounds in carbon tetra-

chloride and dichlorodifluoromethane solutions. He used a well-designed closed generator (see table 2 below), and when carbon tetrachloride was the solvent, a fluorination vessel of special design, made entirely of pure nickel (see figure 1). It consisted of a cylindrical container, equipped with a well-

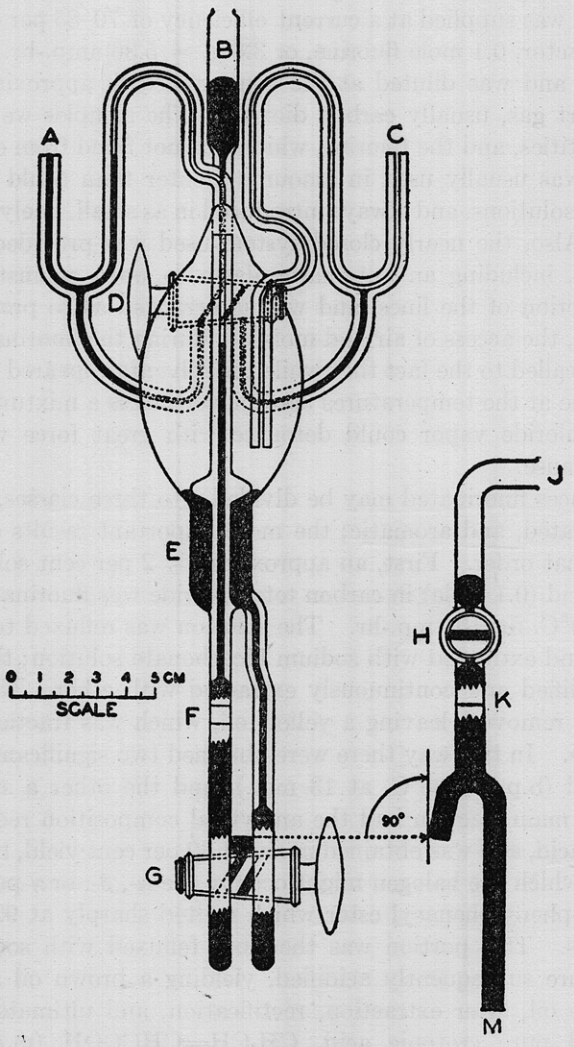


FIG. 1. Apparatus for the direct fluorination of organic compounds in carbon tetrachloride solution (Bockemüller).

fitting lid, which carried both a short exit tube and a long central inlet lead, to which were attached several parallel baffle plates, as shown. These were so arranged that the incoming fluorine, rising from below, would be caught under each plate for more or less time, and so maintained in contact with the solution as long as possible, since the gas was but slightly soluble in it. On the other

hand, when dichlorodifluoromethane was used as solvent, the reactions were carried out in an ordinary glass flask, cooled to about −80°C., either from the outside, or by solid carbon dioxide contained in the solution, in which case the flask was suitably insulated. The solvent was condensed into the flask from a cylinder, and the gas led in through a nickel tube.

The fluorine was supplied at a current efficiency of 70–85 per cent (calculated, without this factor, 0.1 mole fluorine, or 3.8 g. = 5.36 amp.-hr., using a current of 4–5 amp.), and was diluted at the generator with approximately an equal volume of inert gas, usually carbon dioxide. The samples were often used in 0.1 mole quantities, and the fluorine, which was not freed from entrained hydrogen fluoride, was usually used in amounts greater than could be absorbed by the respective solutions, and always introduced in as small, finely divided bubbles as possible. Also, the nearly closed system used was provided with adequate safety devices, including an automatic alarm to warn against rising pressure due to obstruction of the lines, and was so arranged as to prevent, to a great extent at least, the access of air and moisture during the fluorinations. Finally, attention was called to the fact that while the solvents appeared to be practically inert to fluorine at the temperatures used, nevertheless a mixture of fluorine and carbon tetrachloride vapor could detonate with great force without warning or apparent cause.

The substances fluorinated may be divided into three classes,—namely, saturated, unsaturated, and aromatic; the more important results obtained will be described in that order. First, an approximately 2 per cent solution by weight of *n*-butyric acid (0.1 mole) in carbon tetrachloride was fluorinated in the nickel apparatus at 0°C. for 10 amp.-hr. The solution was refluxed to remove hydrogen fluoride, and extracted with sodium bicarbonate solution; then the aqueous layer was acidified and continuously extracted with ether. Next, the solvent was dried and removed, leaving a yellow oil, which was fractionated under reduced pressure. In this way there were obtained two significant portions, one a colorless liquid (b.p. 80–98°C. at 13 mm.), and the other a small brown oily residue. The main fraction had the analytical composition required by monofluorobutyric acid, and was obtained in about 30 per cent yield, but it was clearly a mixture, in which the halogen might occupy the α-, β-, or γ-position, although it yielded a *p*-phenylphenacyl ester which melted sharply at 92°C. after many crystallizations. This portion was therefore refluxed with sodium hydroxide, and the mixture subsequently acidified, yielding a brown oil and an aqueous solution. The oil, after extraction, rectification, and ultimate crystallization, finally yielded pure crotonic acid, $CH_3CH{=}CHCOOH$ (m.p. 72°C.). The solution, believed to contain butyrolactone, was oxidized with bichromate and sulfuric acid, and finally yielded, after suitable purification, pure succinic acid, $HOCOCH_2CH_2COOH$ (m.p. 183°C.). These findings, respectively, furnished quite convincing evidence that the original monofluorobutyric acid consisted of a mixture of the β- and γ-isomers. Finally, pure α-fluorobutyric acid was synthesized by the indirect fluorination of the corresponding α-bromo ester with a mixture of silver fluoride and calcium fluoride at about 150°C. This acid

yielded a pure *p*-phenylphenacyl ester, which, although it melted at 91.5°C., was not identical with the corresponding derivative obtained before; this result makes it probable, but not entirely certain, that the monofluorobutyric acid mixture did not contain any of the α-isomer.

The small oily residue from the distillation of the original crude product was considered of interest, since it finally solidified and on purification yielded pure succinic acid (m.p. 184°C.). From this it was concluded that the fluorination must have produced some of the compound $CF_3CH_2CH_2COOH$, which, on working up, was hydrolyzed to succinic acid. This is extremely unlikely however, on account of the great stability of the resonating $—CF_3$ group which is now well established. It would seem probable that this succinic acid might have been formed from the oxidation of butyrolactone or of the corresponding hydroxy acid by peroxides produced by the action of the fluorine on the carboxyl group of the original butyric acid.

n-Butyryl chloride, and the mixed *n*-butyric acetic anhydride, when fluorinated under approximately the same conditions gave essentially the same results as the free acid; but in contrast, isobutyric acid yielded a crude fraction (b.p. 76–84°C. at 13 mm.) which, on further distillation, furnished analytically pure β-fluoroisobutyric acid (b.p. 80–82°C. at 13 mm.). Since this compound could readily be brominated by the Hell–Volhard–Zelinsky method, in which only the α-position of a carboxylic acid is attacked, it was clear that in this case the β-position was the only one remaining for the fluorine atom.

From work with butyric acid and its derivatives, Bockemüller quite properly concluded that the mechanism of fluorination, which led only to β- and γ-substitution, must be fundamentally different from that of chlorination or bromination, which in like circumstances leads mostly to α-substitution.

Two other saturated aliphatic compounds studied were cyclohexane and *n*-hexadecane, $C_{16}H_{34}$ (m.p. 15–16°C., b.p. 150–155°C. at 13 mm.). The former (0.12 mole) was fluorinated in dichlorodifluoromethane solution (7 per cent) in the glass apparatus at −80°C. for 10 amp.-hr. After the evaporation of the solvent the residual oil was steam distilled, fractionated, and finally yielded analytically pure fluorocyclohexane, $C_6H_{11}F$ (b.p. 100°C.) in about 33 per cent yield. This compound was described as being very unreactive. The second hydrocarbon (0.044 mole) was halogenated in carbon tetrachloride solution (2 per cent) in the nickel vessel at 15°C. for 10 amp.-hr. Then the mixture was washed with sodium bicarbonate solution, dried, and the solvent removed, leaving a yellow oil which was fractionated at reduced pressure. The final product (m.p. about 7°C., b.p. 104–112°C. at 0.2 mm.) had an analytical composition close to that required by the monofluoro derivative, $C_{16}H_{33}F$, and undoubtedly consisted of a mixture of isomers.

Turning now to the unsaturated compounds studied, an approximately 17 per cent solution of tetrachloroethylene (0.18 mole) in dichlorodifluoromethane was fluorinated at −80°C. in the glass apparatus with continuous stirring for 16 amp.-hr. The yellow oil remaining after the evaporation of the solvent was first refluxed to remove unstable and volatile impurities, and then washed with

alkali, dried, and fractionated, in part at reduced pressure. In this way three significant portions were obtained which boiled at 87–93°C., 30–50°C. (13 mm.), and 139–142°C. (13 mm.). The first of these, which mostly solidified at room temperature, was the chief product of the reaction, and after further fractionation yielded analytically pure $CFCl_2CFCl_2$ (m.p. 26.5°C., b.p. 91°C.), which was the expected product. The second portion, present only in small amount, also largely solidified on cooling, and after recrystallization melted at about 100°C. This sample on sublimation yielded analytically pure CCl_3CFCl_2. Both of these were known compounds, having been originally synthesized by Booth, Mong, and Burchfield (14), and had a characteristic odor similar to that of camphor. The former substance has been obtained in an exceptionally high state of purity (m.p. 28.1°C., b.p. 91.50°C. $\pm$ 0.05° by Horvorka and Geiger (44)). The third fraction, a colorless oil which was formed in considerable amount, consisted of the analytically pure dimer, $C_4F_2Cl_8$ (b.p. 139–142°C. at 13 mm.), which, under the circumstances, was in all probability 1,4-difluoroöctachlorobutane, $CFCl_2$-$CCl_2CCl_2CFCl_2$, although this structure was not proved by direct chemical evidence.

Next, a practically 5 per cent solution of crotonic acid ($CH_3CH{=}CHCOOH$) (0.23 mole) in carbon tetrachloride was fluorinated at 0°C. in the nickel apparatus for 10 amp.-hr. The gas was completely absorbed in this case, and a moderate evolution of hydrogen fluoride took place. After removal of the solvent, the crude product was distilled at reduced pressure, and yielded a colorless distillate (b.p. 80–115°C. at 13 mm.), which mostly solidified, and a large brown oily residue.

The former product, which contained large amounts of unreacted crotonic acid, was strongly oxidized with concentrated nitric acid, and the product, after an ether extraction of its solution in alkali to remove neutral impurities, was finally recovered from an acid solution by a second ether extraction. The partially purified acid was then distilled at reduced pressure and yielded crude α,β-difluorobutyric acid (b.p. 90–115°C. at 13 mm.) in about 14 per cent yield. This material was now refluxed with pyridine, again recovered, and refractionated at reduced pressure. This time two significant portions were obtained, which boiled at 90–105°C. (mostly 100–102°C.) and 105–110°C. at 13 mm. The first of these, after final purification by repeated oxidation with nitric acid until it was stable to permanganate, yielded an analytically pure, colorless liquid, $CH_3CHFCHFCOOH$, which would not solidify at 0°C., but was still contaminated by small amounts of its solid stereoisomer. The second fraction, which solidified on cooling, finally yielded after several crystallizations a relatively small amount of analytically pure, white, crystalline $CH_3CHFCHFCOOH$ (m.p. 81°C.), which was also unaffected by alkaline permanganate solutions. The structure of this compound was further substantiated by refluxing it with aqueous sodium hydroxide, which readily converted it into analytically pure, white, crystalline α-fluorocrotonic acid, $CH_3CH{=}CFCOOH$ (m.p. 112°C.), as would be expected.

The large oily residue from the original distillation of the fluorinated crotonic acid was shown to consist largely of a dimeric difluorodicarboxylic acid, presum-

ably having the composition required by the formula $C_8H_{12}O_4F_2$. It was esterified with methyl alcohol, but since the ester could not be completely purified by distillation, it was saponified with alcoholic alkali, which also removed all the fluorine, leaving an unsaturated dimeric acid. This product, after crystallization, melted at 240–244°C. (with decomposition) and gave analytical figures corresponding to the formula $C_8H_{10}O_4$, but the exact structure was not determined.

Oleic acid (0.1 mole) was also fluorinated in 7 per cent solution in carbon tetrachloride at 15°C. in the nickel vessel for 10 amp.-hr., all the gas being absorbed and some hydrogen fluoride evolved during the process. After the removal of the solvent, the oily residue partially solidified, and, on filtration in the cold, yielded a small quantity of crude crystals; these crystals, on repeated recrystallization from ligroin (70°C.), finally yielded analytically pure 9,10-difluorostearic acid (m.p. 81°C.), which was stable to alkaline permanganate solution. In one run, repeated fractional crystallization yielded a small quantity of an analytically pure stereoisomer of this compound, melting at 84–85°C. and not identical with the compound melting at 81°C.

Turning next to the fluorination of aromatic substances, Bockemüller was confronted with a more difficult problem. Benzene, bromobenzene, *p*-dibromobenzene, *m*-dinitrobenzene, quinone, 1,3,5-trinitrobenzene, and 2,4,6-trinitrotoluene gave no definite results, while benzoic acid, fluorinated in the nickel apparatus, yielded only an amorphous, polymeric solid mixture of variable composition, containing about 30 per cent of fluorine and decomposed even by carbonate solution, together with lachrymatory oils, resin, and unchanged sample. Since these phenomena appeared to be caused by polymerization, it was decided to inhibit this process by saturating any reactive intermediates present with bromine. Accordingly, an approximately 2.5 per cent solution of benzoic acid (0.08 mole) was treated with 0.12 mole of bromine, and fluorinated in the nickel apparatus at 0°C. for 15 amp.-hr., with the evolution of hydrogen fluoride. After removal of the bromine, the mixture was extracted with bicarbonate solution, the solvent removed under reduced pressure, and the oily residue steam-distilled, yielding a yellow, pungent, lachrymatory oil which was then repeatedly fractionated. In this way two significant liquid fractions were obtained, which boiled at 110–120°C. and 150–160°C. at 13 mm. and had analytical compositions not far from those required by the formulas $C_6H_6F_4Br_2$ and $C_6H_6F_3Br_3$, respectively. Relatively little polymerization occurred under these conditions, and the products seemed to be halogen derivatives of cyclohexane, formed by the direct addition of both fluorine and bromine to the aromatic nucleus, accompanied by the elimination of the carboxyl group. Accordingly, an attempt was made to aromatize some of the material by heating it with a zinc–copper couple. No definite results were obtained, except that the final product seemed to undergo nitration in preference to oxidation when treated with a nitrating mixture. This work constitutes the first fairly definite evidence that the primary attack of elementary fluorine on the aromatic nucleus is one of addition, rather than substitution.

The investigation which has just been outlined, which seems to have been

summarily cut off by the events leading up to the recent war, represents not only an extensive, but also a markedly significant contribution to the field, and undoubtedly constitutes the most definite advance made up to this time by an organic chemist. It is characterized throughout by the solid analytical support and careful attention to detail which create confidence that the results which have been reported are substantially correct. It is to be regretted, however, that the investigator apparently did not have at his disposal certain types of equipment, such as modern highly efficient fractionating columns, by means of which the results obtained with difficult mixtures could have been considerably extended and improved. The more theoretical aspects of Bockemüller's work will be discussed further in Section III.

H. BIGELOW, Pearson, Cook, Miller, Calfee, Fukuhara, Young, Hadley: fluorination of hexachlorobenzene, hexachloroethane, tetrachloroethylene, ethane, methane, ethyl chloride, acetone, and benzene (mostly in the vapor phase)

The present writer and his students entered the field of organic fluorinations in 1933, in effect simultaneously with Bockemüller. In an introductory paper Bigelow, Pearson, Cook, and Miller (7) described the action of fluorine as produced by a Mathers type of generator on a number of aromatic compounds, such as toluene, naphthalene and its derivatives, and benzil, among others. They used copper apparatus for the most part, and carried out the reactions (*1*) in carbon tetrachloride solution or in suspension at 0°C. under ordinary conditions, and (*2*) with a pure liquid or a carbon tetrachloride suspension at 0–25°C., in the absence of any appreciable vapor phase. Under such conditions the fluorinations were readily controlled and proceeded in a smooth and regular manner. No new compounds were isolated in this study, but a number of significant observations were recorded, as follows: First, the fluorine liberated chlorine from carbon tetrachloride even at 0°C., with the formation of a chlorinating mixture sufficiently powerful to convert toluene ultimately into hexachlorobenzene in considerable yield. Second, the fluorine attacked the aromatic nucleus by an essentially different mechanism from chlorine, often yielding polymerized products which were sensitive to very dilute alkali but extremely resistant to acid oxidizing agents, even hot fuming nitric acid. Third, the fluorine could be passed directly through a liquid hydrocarbon without violent reaction, provided there was no appreciable vapor phase present; nevertheless partial combustion occurred, yielding only hydrogen fluoride and free carbon. Also, the course of the various reactions was followed by numerous analyses, which indicated that the solid polymeric products obtained from naphthalene, benzil, and their derivatives contained roughly 25–60 per cent of fluorine. Finally, it was noted that neither simple nor substituted phthalic or benzoic acids were obtained from these products on strong oxidation, indicating not only that both rings were always involved, but also that the process could hardly have been ordinary substitution. Subsequently much of this preliminary work has been well substantiated, and the fact that the primary attack of fluorine on the aromatic nucleus consists not of substitution but presumably of addition, as postulated by Bockemüller (see above) at the same time, has become practically certain.

Bigelow and Pearson (6) then undertook the fluorination of hexachlorobenzene, C_6Cl_6, a symmetrical, negatively substituted, relatively unreactive aromatic compound containing no hydrogen, which seemed well suited to the purpose. At first, an approximately 6 per cent suspension of the sample (0.18 mole) in carbon tetrachloride was fluorinated in a glass apparatus at 0–20°C. for 105 amp.-hr., after which the clear solution was washed, dried, and the solvent removed, leaving a crude, highly complex liquid product in about 60 per cent yield by weight. This material was accumulated, distilled, and a portion finally fluorinated directly, without solvent, in a metal outfit, for a total of 133 amp.-hr. more. During the process, which took place smoothly and was designed to carry the reaction to completion as far as possible, the sample was subjected to further rectifications, and two significant fractions, one weighing 30 g. (b.p. 100–115°C. at 7 mm.) and one weighing 62 g. (b.p. 135–160°C. at 1 mm.), were collected. When small samples of these oils were emulsified with water and allowed to stand in the cold, solids separated, which, after further purification from dilute alcohol, melted at 94–96°C. and 113–114°C., respectively, and had analytical compositions corresponding closely to those required by the formulas $C_6F_4Cl_6$ and $C_6F_6Cl_6$. This was considered to be the first definite evidence in favor of the addition hypothesis. In comment it is only fair to say that while this evidence appears legitimate, the analytical samples represented only a minute proportion of the materials involved, and the part played by the water in the solidification has not yet been determined with certainty. Also, the evidence presented by Bockemüller (see above) in support of the same postulate, even though he did, to be sure, use fluorine and bromine together, is at least equally convincing.

By this time several important factors involved in these reactions had been recognized: namely, that fluorine produced by a Mathers-type generator was often highly contaminated with other gases; that this halogen reacted with almost any organic solvent, frequently including carbon tetrachloride even at relatively low temperatures if in the presence of an organic solute; and finally, that all direct fluorinations seemed to yield highly complex reaction products. In fact, it appeared probable that during the course of a fluorination in carbon tetrachloride there might well be present, in addition to the fluorine, the solvent, the solute, and the reaction products, such substances as oxygen, oxygen fluoride, chlorine, chlorine fluoride, and hydrogen fluoride as well as others in lesser amounts. It was hardly surprising that the earlier results had been baffling and often disappointing. Accordingly, Miller and Bigelow (60) (see below) designed and placed in service a new closed generator, shown to deliver fluorine (94–99 per cent pure by analysis) at an average electrical efficiency not far from 80 per cent. Also, it was decided to fluorinate in the vapor phase, thus avoiding the use of solvents altogether, and to study simpler molecules, in the hope of obtaining less complex products.

On this basis, Miller, Calfee, and Bigelow (61) carried out the vapor-phase fluorination of hexachloroethane (C_2Cl_6) over a copper-gauze catalyst, by a modification of the procedure originally described by Fredenhagen and Cadenbach (33) (see below). It was expected that the heat-conducting metal would

moderate the reaction by reducing local overheating, and that the presence of a surface layer of cupric fluoride might promote the change. The simple apparatus consisted of a glass tube heated by sliding air baths. Fluorine from the closed generator, at the rate of about 1.5 liters per hour and diluted with nitrogen in the molar ratio of 1:1.6, entered the reactor at one end through the meshes of a tightly wound copper-gauze roll. Beyond this came the solid sample, which was followed by a second similar roll, and the products passed out of the tube at the other end, where they were condensed by a freezing mixture. In operation, the second gauze was heated, then the first, and finally the sample was progressively sublimed into the fluorine, where it reacted smoothly and steadily. The crude liquid product, condensed at the rate of 1.6 g. per hour, or 75 per cent by weight of the hexachloroethane consumed, was washed, dried, rectified in a Podbielniak still, and finally gave a 20 per cent yield of pure *s*-difluorotetrachloroethane, $CFCl_2CFCl_2$ (m.p. 24–25°C., b.p. 92°C.). This known compound had the correct analytical composition and physical constants, making its identity certain. This reaction was the first case to be described in which the vapor-phase fluorination of an organic compound containing more than one carbon atom yielded a pure, individual product.

In addition, it was found that when the vapor of tetrachloroethylene (C_2Cl_4) was carried into the same apparatus on a current of nitrogen, and fluorinated over the copper-gauze catalyst, the same compound was formed, as would be expected, the yield being also 20 per cent of the calculated amount.

Since the vapor-phase fluorination of a simple molecule such as hexachloroethane over a metal catalyst had proved both convenient and relatively successful, the next logical step was to apply the procedure to a hydrocarbon, in spite of our earlier conviction that this would lead to violent and uncontrollable reactions. Consequently, Calfee and Bigelow (20) permitted fluorine and ethane to mingle within the meshes of a copper wire-gauze packing, contained in a brass pipe, and so arranged that the halogen entered behind the hydrocarbon in respect to the direction of the gas flow. This very simple device proved surprisingly successful, since the reaction took place smoothly, quietly, and continuously, so long as the reactants were supplied; and neither the relative proportions of the reacting gases, nor their order of mixing, nor even the nature of the sample had any appreciable effect on the general result. In operation, fluorine from the closed generator, at the rate of nearly 2 liters per hour, was mixed with ethane in the approximate molar ratio of halogen to hydrocarbon as 3:2. The gaseous products then passed over sodium fluoride contained in two similar brass pipes in series, to absorb quantitatively all the hydrogen fluoride which had been formed, after which they were condensed by liquid air in a trap carefully protected from air and moisture. The fluorinated ethane, which was formed at the rate of about 1 cc. per hour, was accumulated for 18 hr., passed through alkali, dried, and carefully rectified, using a Podbielniak low-temperature distilling column and a simplified form of the excellent fractionating apparatus described by Booth and Bozarth (13). Finally, three definitely significant fractions were obtained: 4–5 cc. (b.p. −125°C.); 1 cc. (b.p. −88°C.);

and 5–6 cc. (b.p. −78°C.). These fractions were undoubtedly carbon tetrafluoride, unchanged hexachloroethane, and hexafluoroethane, respectively. Two other portions were also described (b.p. −84°C. and −50° to −48°C.), which were believed to be CHF_3 and either CH_3CF_3 or CH_2F_2, respectively. However, the presence of these compounds in the fluorination product has not been confirmed by subsequent work, and it is quite likely that the second portion actually consisted of the then unknown compound CF_3CHF_2, which boils at −48.5°C. The procedure described here gave great promise of general application in the study of organic fluorinations, a promise which has since been amply fulfilled. It also represents the first instance in which a hydrocarbon was acted upon by elementary fluorine to produce a definite, known chemical individual other than carbon tetrafluoride.

Continuing the study of the fluorination of ethane, Calfee, Fukuhara, and Bigelow (21) carried out the reaction using progressively varying proportions of the reacting gases. The apparatus and operation were much the same as before, except that the respective volumes of the reactants were carefully measured or estimated, the catalyst packing was changed to small wire-gauze squares, and the crude condensate, which in most cases contained no free fluorine, was fractionated directly, using the completed Booth–Podbielniak low-temperature fractionating unit. This last consisted of a Podbielniak column equipped with liquid-air cooling, thermocouple, and automatic recorder, a flexible condensing system, melting-point apparatus, and gas-density balance for determining molecular weights during the distillations.

It was found that as the molar ratio of $F:C_2H_6$ varied from 1:1 to 6:1, the relative amounts of carbon tetrafluoride and hexafluoroethane produced increased, and the quantity of recovered ethane decreased as would be expected, but the proportion of partially fluorinated ethanes formed boiling higher than hexafluoroethane (−78°C.) never rose above 30 liquid volume per cent of the total condensate, and was usually far less than this value. Clearly, the reaction would have to be further moderated in intensity before these latter compounds could be isolated and studied. However, two interesting azeotropic mixtures (b.p. −92°C. and −104°C.) were isolated at this time. They were shown to consist of hexafluoroethane and ethane in the approximate molar ratio of 1:2, and of hexafluoroethane, ethane, and silicon tetrafluoride in the ratio of 1:6:1, respectively. The silicon tetrafluoride must have resulted from the action of some unabsorbed hydrogen fluoride on the glass apparatus.

As a result of the preceding work, Young, Fukuhara, and Bigelow (92) undertook a study of the influence of progressive nitrogen dilution on the fluorination of ethane, in order to moderate the reaction and to secure greater amounts of the partially fluorinated ethanes as products. The apparatus and procedure remained unchanged, except that measured amounts of diluent nitrogen were introduced into the fluorine line. The crude liquid-air condensate, usually obtained at the rate of 1.5–2.3 cc. per hour and well protected from air and moisture, was rectified in the Booth–Podbielniak unit. After many runs at molar fluorination ratios ($F_2:C_2H_6$) of 2:1 and 4:1, and dilution ratios ($F_2:N_2$) ranging

from 1:1 to 1:20, it was found that when the former was 4:1 and the latter 1:3, corresponding to a reaction ratio (F_2:C_2H_6:N_2) of 4:1:12, the proportion of partially fluorinated ethanes formed rose to 90 liquid volume per cent of the total condensate. Under these conditions, the fluorination product contained no hexafluoroethane, no unchanged ethane, and but little carbon tetrafluoride. The material boiling above −78°C. was then accumulated, and repeatedly rectified with great care and at various pressures. Finally, pure CF_3CHF_2 (m.p. −103°C., b.p. −48.5°C.), CHF_2CHF_2 (b.p. −23.5° to −22.5°C.), and CHF_2-CH_2F (m.p. −84°C., b.p. −3°C.) were isolated from the complex mixture. Of these all gave correct analytical figures and molecular weights, but only the first was a new compound, the others having been made earlier by indirect methods. These results showed definitely that the vapor-phase fluorination of ethane under mild conditions yields, in addition to carbon tetrafluoride, hexa-, penta-, tetra-, and trifluoroethanes, but it is also of interest that none of the corresponding mono- or disubstitution products could be detected in the mixture. It is known, however, that the compounds CH_3CH_2F and CH_2FCH_2F are to some extent thermally unstable, which may account for the fact that they were not formed, but this is speculative and would hardly account for the fact that CH_3CHF_2 did not appear to have been formed either. In this connection, it should be noted that in all of these experiments no attempt was made to control either the temperature of the reactor packing or the rate of flow of the gases through it, both of which factors would presumably have a significant influence upon the final results.

Since this reaction had yielded satisfactory results with ethane, the next logical development was obviously a study of the corresponding fluorination of methane, which had not been attempted first because preliminary experiments had indicated that it would involve complications, in spite of the simple and fundamental structure of the hydrocarbon. Accordingly, Hadley and Bigelow (40) carried out the methane fluorination, over the copper-gauze catalyst, under essentially the same conditions as have just been described, using progressively varying molar ratios of the reacting and diluent gases. It was found that when the fluorination ratio was 2:1, the dilution ratio 1:5, and thus the reaction ratio 2:1:10, the proportions of the product boiling higher than carbon tetrafluoride (−128°C.) rose to a maximum of 45 liquid volume per cent of the total condensate. It was impracticable to increase the dilution ratio still further, since under such conditions it was not easy to condense the low-boiling gases efficiently. This complex higher-boiling material, consisting of partially fluorinated methane and other products, was accumulated, passed repeatedly through alkali to remove carbon dioxide and silicon tetrafluoride, dried, and rectified in the improved Booth–Podbielniak unit. The results, to us at least, were quite surprising, since essentially no pure chemical individuals came over in the original distillations, even though some of the expected products were known to boil 30°C. apart. Instead, there were obtained in satisfactory yields from the several accumulations prepared under different operating conditions, three distinct, reproducible, heterogeneous, and therefore constant-boiling mixtures with con-

stant molecular weights: b.p. −89°C. (mol. wt. 94), b.p. −89°C. (mol. wt. 85), and b.p. −58°C. (mol. wt. 95), together with considerable amounts of as yet unidentified products. These mixtures, either in combination or individually, were separated by freezing the lower layers, then boiling off the supernatant liquids, and finally rectifying each separately. By this means, the first mixture was shown to consist of fluoroform (b.p. −82°C.) and hexafluoroethane (b.p. −79°C.); the second of difluoromethane (b.p. −52°C.) and octafluoropropane (b.p. −36°C.); and the third of methyl fluoride (b.p. −78°C.) and hexafluoroethane (b.p. −79°C.). All of these compounds, which were already known, were satisfactorily isolated in pure condition and identified. Thus the fluorination of methane has been shown to yield, not only all of the expected fluoromethanes, but hexafluoroethane and octafluoropropane as well. This interesting result has demonstrated beyond doubt that a vapor-phase fluorination under the conditions described can not only effect the expected substitutions, but also may build up a carbon chain. This polymerization, which is associated with the free-radical or atomic nature of the reactions, has since become increasingly important.

While these experiments with hydrocarbons were going on, the fluorination of chlorinated compounds had not been entirely neglected. Fukuhara and Bigelow (35) progressively sublimed hexachlorobenzene (C_6Cl_6) from a side arm heated to 189–195°C. into a glass reaction chamber where it mingled and reacted smoothly at 55°C. and atmospheric pressure with a current of fluorine issuing through the meshes of a copper-gauze roll at the rate of about 2 liters per hour. The crude product, which was a heavy, yellow, fuming oil, condensed continuously on the walls, ran out at the bottom, and collected in a receiver below at the rate of about 8 g. per hour as long as the reactants were supplied. In general, for each 25 g. of sample consumed, 27 g. of the oil was formed; and this product, which contained roughly 13 per cent fluorine and 53 per cent chlorine, was essentially inert to fluorine, even when the gas was bubbled directly through it. The oil was considered too reactive to handle, so it was powerfully reduced by refluxing with iron powder in acetic acid solution, followed by steam distillation, in the hope of aromatizing and stabilizing it, even though a large part of the sample was destroyed in the process. The partially purified material then consisted of stable colorless liquid and some crystalline solid, which were accumulated. The oil, after washing with dilute alkali, was rectified in a high-temperature Podbielniak fractionating unit, and the solid repeatedly crystallized. As a result, no less than ten liquid and two crystalline portions were isolated, which were considered to be chemical individuals, and which possessed a number of more or less remarkable characteristics. First, all significant portions of the distillation curve, as well as the appearance of the solids, were strictly reproducible; next, all ten of the liquids, boiling constantly at various points between 32° and 75°C. at 11 mm., and the two crystalline solids (m.p. 69–70°C. and 142–143°C., respectively) contained fluorine and chlorine by analysis in atomic ratios of Cl:F corresponding to simple whole numbers; and finally, the crystals had sharp melting points, while six of the liquids had sharp freezing points, as

indicated by the freezing curves, the others becoming glasses on cooling. No molecular weights, nor evidence as to the structures of the compounds, were presented.

By way of comment it may be said that it seems quite likely that the samples with both constant melting and boiling points, and Cl:F ratios as simple whole numbers as well, were actually pure chemical individuals. However, all of this material, chemically speaking, was a long way from its starting point, and probably consisted of highly halogenated, partially polymerized fragments, originally formed owing to the primary saturation and subsequent splitting of the aromatic ring by the fluorine, some of which were known to contain oxygen, and perhaps hydrogen as a result of acetolysis and hydrolysis during the stabilization process. These findings illustrate still more clearly the wisdom of studying simpler molecular species first; nevertheless the writer believes that we have shown enough to suggest that the fluorination of hexachlorobenzene offers an interesting and also a challenging field for further research.

With the preceding experience in mind, and the satisfactory technique for reacting gaseous hydrocarbons with fluorine available (see above), Calfee, Fukuhara, Young, and Bigelow (22) next studied the vapor-phase fluorination of the simple alkyl halide, ethyl chloride (b.p. +12°C.), over a copper-gauze catalyst in the manner already described. In this case, contrary to previous experience, the catalyst deteriorated rapidly unless maintained anhydrous between runs. The products were condensed by liquid air, accumulated, transferred to the Booth–Podbielniak still, and rectified in the usual way, except that the material boiling above +12°C. was withdrawn, washed with alkali, and distilled from an ordinary flask. There were formed in substantial amounts CF_4, CF_3Cl (b.p. −80°C.), CF_3CF_2Cl (m.p. −106°C., b.p. −38°C.), $CF_2{=}CCl_2$ (m.p. −116°C., b.p. 0°C.?), and CHF_2CH_2Cl (b.p. 35°C.). All of these had the correct molecular weights; the last four were analyzed and gave correct figures for both fluorine and chlorine. In addition, some evidence was found for the presence of the compounds CHF_2CHCl_2 and CH_3CHCl_2 in the complex reaction product. Locke, Brode, and Henne (55) have prepared the compound $CF_2{=}CCl_2$ by indirect methods, and after carefully checking this work, Henne and Wiest (43) have found the compound to boil at 18.9–19.0°C., a value much more nearly in line with the boiling points of related halogen compounds than 0°C. The present writer has been creditably informed that the higher value for the boiling point of $CF_2{=}CCl_2$ has recently been confirmed by others, but this work has not as yet been published. Up to the present time, the reason for the discrepancy has not been determined. In this fluorination of an alkyl chloride it is of interest that not only the expected substitution and fragmentation took place, but apparently chlorination as well; this may have been due to the presence in the reacting gases of significant amounts of chlorine fluoride, formed, presumably, by the direct displacement of chlorine by fluorine.

Since the vapor-phase fluorination of organic gases had been markedly successful, the next, and obvious, step was to adapt the process to volatile liquids in a heated reactor; so Fukuhara and Bigelow (36) fluorinated acetone, using the

improved outfit illustrated to approximate scale in figure 2. This apparatus consisted essentially of the vertical, heated, screen-packed reactor (C), calibrated glass capillary (D), sump (K), heated tubes (L and L′) containing sodium fluoride to absorb hydrogen fluoride, and well-protected glass cold trap (M). In operation the sample under air pressure in A entered the reactor which was originally heated to 60°C. through D and G, while the fluorine was led in simultaneously through H and I. The more volatile products passed out at the top, were freed from hydrogen fluoride in L and L′ and finally condensed in M, while less volatile materials ran out at the bottom and were collected in K at the same time. The samples were accumulated, rectified, and finally yielded CF_4, COF_2 (b.p. −83°C.), CF_3COF (b.p. −59°C.), CF_3COCF_3 (m.p. −129°C., b.p. −28°C.), $(COF)_2$ (b.p. 26°C.), CH_2FCOCH_3 (b.p. 78°C.), and other unidentified substitu-

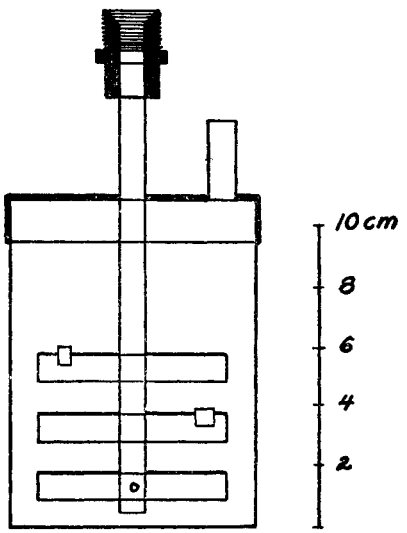


FIG. 2. Apparatus for the vapor-phase fluorination of volatile organic liquids

tion and condensation products. The known compounds COF_2, CF_3COF, and CH_2FCOCH_3 were further identified by conversion to diethyl carbonate, trifluoroacetamide, and the corresponding semicarbazone, respectively, while the new CF_3COCF_3 and $(COF)_2$ as well as the CH_2FCOCH_3 were analyzed and gave the correct figures. In addition, the hexafluoroacetone was soluble in water, stable in solution, and yielded a crystalline semicarbazone (m.p. 153°C. (decomposition)), while the oxalyl fluoride could be converted readily into the expected oxamide. It will be noticed that in this interesting reaction there were formed, not only the completely fluorinated molecule, but also the expected fragmentation products and the unexpected dimer, oxalyl fluoride. Incidentally, the boiling point of the known monofluoroacetone has been corrected. Since the procedure used was quite general, this development made possible the vapor-phase fluorination of any readily volatile organic liquid.

With a good process for the fluorination of volatile organic liquids at their disposal, Fukuhara and Bigelow (37) in 1941 next undertook a study of one of the most important of such compounds—namely, benzene itself—in spite of the fact that this hydrocarbon could scarcely be classed as having a really simple structure. They employed the same apparatus and techniques which have been described. Using a molar reaction ratio of $F:C_6H_6:N$ as 4:1:2, with the fluorine being supplied at 1.7 liters per hour and the reactor maintained at 90°C., they obtained a clean, but complex crystalline product condensed by liquid air at the rate of about 1.1 cc. per hour. This product always contained an excess of benzene, and corresponded roughly to 40 cc. of fluorinated material per 100 hr. of operation, during which time some 4–5 g. of tar was deposited inside the reactor.

A large amount of the crude product was collected and carefully rectified in Booth–Podbielniak stills, the distillation curves being strictly reproducible throughout. There resulted four pure compounds, CF_4, C_2F_6, C_3F_8, and C_4F_{10} (b.p. −2°C.), with the exception of the first, in small amounts; and four significant constant-boiling mixtures, b.p. 22°, 48°, 61–63°, and 79°C., respectively, all of which contained unreacted benzene. The first mixture was heterogeneous, carried but little hydrocarbon, and was separated by distillation with *n*-pentane. This operation brought over a new heterogeneous mixture (b.p. −5° to −3°C. at 330 mm.), the lower fluorocarbon layer of which on final rectification yielded pure saturated C_5F_{10} (b.p. 0–1°C. at 330 mm., or 22°C. at atmospheric pressure). The next mixture, also heterogeneous and obtained in the greatest amount, carried a much greater proportion of benzene, so the layers were separated mechanically. The lower, fluorocarbon layer was then distilled at 218 mm. until the contents of the column solidified, and the distillate was discarded. After this the residue, mostly solid, was further purified by distillation from trap to trap at low pressures, and finally refractionated in a special still at atmospheric pressure, yielding pure C_6F_{12} (m.p. 48–49°C., b.p. 50°C.) with a liquid range of less than 2°C. This melting point, which is somewhat difficult to attain, was extremely sensitive to the merest trace of benzene in the product. The third mixture was homogeneous, was apparently azeotropic, and contained much benzene. The sample, in combination with other similar material, was then distilled with an excess of C_6F_{12}, which brought over the heterogeneous mixture boiling at 48°C. (see above), until all of the hydrocarbon had been removed. Subsequent careful rectification of the mixture yielded pure C_6HF_{11} (b.p. 62°C.) and left a higher-boiling, unidentified residue. The last mixture was again heterogeneous, and consisted mostly of benzene. The lower, fluorocarbon layer was separated, accumulated, and rectified in a special still, yielding chiefly pure $C_{12}F_{22}$ (m.p. in bulk 19–21°C., b.p. 90°C. at 90 mm.).

Summing up, the fluorination of benzene yielded CF_4, C_2F_6, C_3F_8, C_4F_{10}, C_5F_{10}, C_6F_{12} (in greatest amount), C_6HF_{11}, and $C_{12}F_{22}$, but no aromatic fluoro compounds could be found. All of these products, except the well-known first three, were analyzed and gave the correct figures. The C_6HF_{11} and $C_{12}F_{22}$ were entirely new, and it is not at all certain that the C_4F_{10}, C_5F_{10}, and C_6F_{12} which

had been described previously by Simons and Block (87) possessed either the same structures, or even the same exact compositions as ours. The results as a whole were considered to constitute strong evidence that the attack of elementary fluorine on the aromatic nucleus proceeds by an atomic chain mechanism, involving first addition, then substitution, and finally fragmentation, followed to some extent by polymerization. The detailed mechanisms discussed in this and the preceding papers will be considered more fully in Section III.

The writer cannot, in the nature of things, appraise the value of the work done under his own direction, but he would like to take this opportunity to express his gratitude for, and appreciation of the ideas, skills, perseverance, and loyalty of his student collaborators, without whom such progress as was made would not have been possible.

I. FREDENHAGEN, Cadenbach, Krefft: fluorination in the presence of a metal screen; fluorination of as-diphenylethylene

In 1934, not long after the work which has just been outlined had been started, the physical chemist Karl Fredenhagen, whose fluorine generator will be described in detail below, made a brief, but significant entrance into the field of organic fluorinations. In a paper by Fredenhagen and Cadenbach (33), in which the experimental portion is credited chiefly to the junior author, there was described for the first time a new method for moderating and controlling such reactions. The simple apparatus used consisted essentially of a horizontal, well-cooled, and rapidly rotating glass cylinder. A stationary copper inlet tube entered this rotor at one end, and extended along its central axis for about half the length of the cylinder, which was open to the air at the opposite end. The tube was closed at the inner end, but was filled with numerous perforations along its length, and wrapped with several layers of copper gauze. In operation the liquid sample was spread in a thin layer over the inner wall of the cylinder by centrifugal force, while the fluorine entered through the meshes of the gauze and reacted smoothly, without combustion, either in the vapor phase, accompanied by faint glowing, or at the large liquid surface when the sample had a low vapor pressure. In this way such compounds as benzene, toluene, paraffin oil, and palmitic acid were easily fluorinated; while no pure fluorine compounds were isolated, materials were collected which contained from 9–58 per cent of fluorine by analysis. It was of interest that when a glass inlet, even when provided with fine perforations, was used, the reactions were not moderated and consisted for the most part of combustion. Subsequently, a considerably elaborated procedure apparently based on these experiments was patented by Krefft (107), but the only definite reaction described was the conversion of $(C_6H_5)_2C{=}CH_2$ into the expected difluoride in good yield.

These experiments were clearly of the exploratory type, which so often seem to be without concrete results; yet in this case they demonstrated that when the direct fluorination of organic compounds was conducted in the presence of a metal screen, the reactions were greatly moderated in intensity and took place to a much lesser extent by combustion. This interesting observation was one

of the important factors leading up to the subsequent successful development of vapor-phase fluorination in the writer's laboratory.

J. SIMONS, Block, Bond, McArthur, Herman: fluorination of carbon, carbon tetrachloride, dichlorodifluoromethane, and acetephenone

It was not until 1937 that Joseph H. Simons, a physical chemist who had been working for many years with fluorine and its compounds, began his studies dealing with direct organic fluorination. In that year Simons and Block (86) published a preliminary communication stating that the reaction of fluorine with carbon had yielded the fluorocarbons CF_4, C_2F_6, C_3F_8, C_4F_{10}, C_5F_{12}, and C_6F_{14}, all identified by their respective molecular weights only. No experimental details were given, except in regard to the fractionation, and the results were later materially modified. Subsequently, Simons and Block (87) gave a detailed report of their findings. They passed fluorine from Simons open generators (84, 85) of the Mathers type over different varieties of finely divided carbon contained in a heated copper tube. About 1 per cent of mercuric chloride or mercurous chloride was added to the charge in order to inhibit the violent explosions which otherwise took place. The exit gases were passed through an alkali solution, rigorously dried, condensed by liquid air, and finally rectified in a low-temperature fractionating unit. No definite information was given concerning the rate of flow of the fluorine or the temperature of the reactor, and it was stated that some of the cuts in the fractionation could not be made sharply. There were formed CF_4, C_2F_6, C_3F_8 (m.p. −183°C., b.p. −38°C.), two isomers of C_4F_{10} (b.p. −4.7°C. and +3.0°C., respectively), C_5F_{10} (m.p. about −12°C., b.p. 23°C.), C_6F_{12} (b.p. 51°C.), and C_7F_{14} (b.p. 80°C.), together with other unidentified fluorocarbon mixtures. The first three of these comprised 55, 13, and 8 liquid volume per cent of the crude product, respectively, while the others were present in smaller amounts, ranging from 1–5 per cent approximately. All of them had not far from the required molecular weights and, with the exception of the first two, were analyzed by decomposition over heated sodium for both carbon and fluorine. The results leave something to be desired as regards precision, but this may have been due to the analytical method, which cannot be relied upon to give precise results for carbon on account of the formation of metal carbides, as pointed out by the authors in one case. Each of the substances analyzed was new, but only the C_3F_8 can be regarded as a pure chemical individual, while the C_5F_{10} may have been approximately such. The other four, which yielded glasses on cooling, were quite likely mixtures of isomers, especially when the pyrogenetic nature of the reaction is considered. Pure C_6F_{12} has since been shown to be a white crystalline solid (m.p. 48–49°C., b.p. 50°C.) (37). Additional support for the structures claimed was given by comparing the properties of the fluorocarbons with those of related hydrocarbons, and also with those of the inert gases. Finally, a number of other physical constants pertaining to the various fractions were reported.

Later, in a paper dealing with compounds containing the CF_3 group and covering a number of both direct and indirect fluorinations, Simons, Bond, and Mc-

Arthur (88) described the fluorination of carbon tetrachloride and dichlorodifluoromethane. They passed fluorine, at the rate of about 0.16 mole per hour, through carbon tetrachloride containing 6.3 per cent by weight of arsenic in suspension and maintained at 70°C. in a special copper flask equipped with a condenser and stirrer. The reaction proceeded quietly, and the exit gases were washed with alkali and collected over water. The product contained 74 per cent of carbon tetrafluoride and only 17 per cent of chlorotrifluoromethane, as compared to 20 and 54 mole per cent of the respective gases obtained earlier by Ruff and Keim (77), using the same reagents and catalyst but somewhat different operating conditions. In the hope of increasing the proportion of chlorotrifluoromethane formed, the experiment was repeated, using only 2.3 per cent of arsenic, but the reaction was too vigorous, and was moderated by adding 2.5–3.3 per cent of bromine, which, as a more active catalyst, was expected to reduce the reaction temperature. However, the effect was greater than anticipated, and the product in this case was nearly pure trichlorofluoromethane. The desired chlorotrifluoromethane was finally obtained in high yield by passing a mixture of fluorine and dichlorodifluoromethane, with the latter in slight excess, over a mercury catalyst contained in a copper tube heated to 340–370°C. The reaction proceeded smoothly, and the product contained essentially no carbon tetrafluoride. Arsenic, silver fluoride, and bromine were ineffective as catalysts under these conditions. Neither physical constants, criteria of purity, nor yields were given in the descriptions of any of these experiments. Incidentally it was observed that the residues from the fluorination of carbon tetrachloride contained hexachlorobenzene (C_6Cl_6), which also results when carbon tetrachloride is passed through a carbon arc. This emphasized the fragmentation and subsequent polymerization which often accompany fluorinations, and also suggested that perhaps all of the hexachlorobenzene obtained in the writer's laboratory when a carbon tetrachloride solution of toluene was fluorinated (7) did not come from the hydrocarbon, as was then supposed.

Subsequently, in a paper devoted chiefly to various indirect fluorinations, Simons and Herman (89) described the action of elementary fluorine on acetophenone. They passed fluorine, diluted with five times its volume of nitrogen, at the rate of 0.2 mole per hour for 5 hr. through a solution of 0.5 mole of acetophenone in 200 g. of liquid hydrogen fluoride at 0°C. contained in a copper reaction chamber equipped with a refrigerated condenser, and so arranged that the fluorine stream was equally divided between two separate inlet tubes. The reaction, which was catalyzed by 2 g. of silver oxide, proceeded quietly, but at the end most of the fluorine passed through unreacted. Then the product was poured onto ice, extracted with ether, and the hydrogen fluoride removed by means of sodium fluoride. Finally the ether solution was dried, the solvent removed, and the product fractionated, yielding 2.1 g. (3.3 per cent) of benzoyl fluoride (b.p. 74–79°C. at 30 mm.) and 15.7 g. (20.2 per cent) of ω-difluoroacetophenone, $C_6H_5COCHF_2$. The former compound was identified by means of the corresponding benzanilide (m.p. 162–163°C.), and the latter by conversion to mandelic acid with 5 per cent sodium hydroxide solution. Neither the boiling range of

the fluorinated acetophenone nor the melting point of the mandelic acid derived from it was given for this preparation, although this same halogen derivative, as prepared indirectly from the corresponding dibromo compound, was adequately characterized (b.p. 83–85°C. at 29 mm.), 2,4-dinitrophenylhydrazone (analyzed) (m.p. 221–223°C.). Also, none of the corresponding mono- or trifluoroacetophenone was formed. This unexpected reaction would appear to indicate that under mild operating conditions, a benzene nucleus may be more resistant to attack by fluorine than has hitherto been believed. Possibly the ring was deactivated by formation of the salt $(C_6H_5COHCH_3)^+F^-$. It is, however, difficult to understand how free fluorine could have passed unchanged through the system containing the acetophenone derivative unless the two were not actually in contact.

The various homologous series of fluorocarbons, the use of catalysts in direct fluorinations, and the conducting of such reactions in anhydrous hydrogen fluoride solution represent interesting and important fields of research, which merit further development.

K. MILLER: fluorination of chloroform, pentachloroethane, s-tetrachloroethane, tetrachloroethylene, and trichloroethylene (all in the liquid phase)

It was in 1940 that the writer noted with satisfaction the entrance into this field of his former student William T. Miller, now an organic chemist of standing in his own right. In a paper of merit Miller (58) described a new procedure for the direct fluorination of organic liquids. The simple apparatus, constructed of brass tubing, was roughly U-shaped, except that the vertical sides were at right angles and there was a flat middle section. The latter was to a large extent divided into upper and lower compartments by a horizontal baffle plate, at one end of which was a small vertical well containing a mechanical stirrer. This was activated through one of the arms of the U and so arranged as to produce a definite flow of liquid around the ends of the baffle and in opposite directions in the two compartments. The arm which carried the vertical stirrer shaft was tightly closed at the top, except for a small exit tube, while the other one carried the fluorine line, which entered through a rubber stopper protected by thin copper foil and was tightly wrapped with a roll of copper gauze at the inner end. In operation, the lower section of the apparatus was filled with the liquid organic sample, while the undiluted fluorine, substantially free from oxygen (60), entered through the wire gauze at the rate of 1.7 liters per hour (5 amp.), bubbled progressively in counter-current flow through the sample, and finally, if unreacted, passed out together with any volatile products through the exit tube adjacent to the stirrer shaft. This method resulted in excellent mixing and smooth reactions, taking place either in the vapor phase or at the liquid surface. The organic samples were always in large excess, and finally served as solvents for the products. These mixtures were in all cases carefully washed, dried, and then repeatedly rectified.

Under these conditions, the fluorination of chloroform ($CHCl_3$) for 15 amp.-hr. at 0°C. gave a crude product essentially 100 per cent by weight of the original

sample, which on fractionation yielded trichlorofluoromethane (b.p. 23–25°C.) equivalent to 5.6 per cent of the crude, and hexachloroethane (m.p. 184°C. (subl.)), 0.5 per cent, as residue after removal of the excess of chloroform. It was observed that this material was too volatile for smooth fluorination by this method, and could be handled more efficiently in a packed tube.

In a like manner pentachloroethane (CCl_3CHCl_2), fluorinated for 50 amp.-hr. at 90°C. ± 3°, reacted smoothly and gave 85 per cent of its weight of crude product, which on rectification yielded $CFCl_2CFCl_2$ (m.p. 22–24°C., b.p. 90–92°C.), 1.7 per cent of the crude; $CCl_2{=}CCl_2$ (b.p. 117.5–118°C.), 5.2 per cent of the crude; CCl_3CFCl_2 (m.p. (redist.) 99.8–100°C., b.p. 137–139°C.), 28 per cent of the crude; and C_2Cl_6 (m.p. 183–184°C. (recryst., subl.)), 9.5 per cent of the crude, together with much unreacted sample. By extraction of the still residue with alcohol, and subsequent crystallization by slow evaporation from glacial acetic acid and formic acid (1:1), there was also obtained analytically pure $CCl_3CCl_2CCl_2CCl_3$ (m.p. 80–81°C.). Similarly, *s*-tetrachloroethane ($CHCl_2$-$CHCl_2$) when reacted for 70 amp.-hr. at 50°C. ± 2° gave 95 per cent of its weight of crude product, which on redistillation yielded $CCl_2{=}CHCl$ plus $CFCl_2$-$CFCl_2$ (b.p. 90–95°C. ?); $CHCl_2CFCl_2$ (b.p. 115.5–116.5°C.), 22 per cent of the crude (redistilled, b.p. 115.7°C.); and CCl_3CHCl_2 (b.p. 159–160°C.), 3.6 per cent of the crude; together with a large amount of unchanged material. The $CCl_2{=}CHCl$ and $CFCl_2CFCl_2$ could not be separated by distillation, but the former was identified as $Hg(CCl{=}CCl_2)_2$ (m.p. 82–83°C.) and the latter was finally obtained slightly impure (m.p. 19–23°C., b.p. 92–93°C.). No hexachloroethane could be isolated from the reaction mixture. Likewise, tetrachloroethylene ($CCl_2{=}CCl_2$) after reaction for 60 amp.-hr. at 0°C. gave 106 per cent of its weight of crude product, which on fractionation yielded $CFCl_2CFCl_2$ (b.p. 89–94°C.) (redistilled, m.p. 24.43–24.73°C. (corr.), b.p. 92.3°C.), 16 per cent of the crude; CCl_3CFCl_2 (b.p. 136–138°C.) (redistilled, m.p. 99–99.5°C. (in a sealed tube)), 14 per cent of the crude; and $CFCl_2CCl_2CCl_2CFCl_2$ (m.p. 4–5°C., b.p. 152.5°C. at 20 mm.), 19 per cent of the crude; along with the unchanged sample.

Next, trichloroethylene ($CCl_2{=}CHCl$), when fluorinated for 50 amp.-hr. at 0°C., gave 102 per cent of its weight of crude product, which on rectification yielded at first a very volatile portion, b.p. up to 40°C., which apparently contained $CFCl{=}CHCl$, identified as $CFClBrCHClBr$ (b.p. 160–162°C.). Then came a mixture (b.p. 71.5–73°C.) presumably consisting of $CFCl_2CHFCl$ (known b.p. 72.5°C.) and $CFCl{=}CCl_2$ (known b.p. 72.1°C.), 4.3 per cent of the crude, which could not be separated, but which yielded on chlorination both $CFCl_2CFCl_2$ and CCl_3CFCl_2. This was followed by another mixture (b.p. 114–116°C.), probably $CHFClCCl_3$ (known b.p. 117°C.) and $CHCl_2CFCl_2$ (known b.p. 116.6°C.), 5.4 per cent of the crude, which could not be separated but which, on chlorination, yielded only CCl_3CFCl_2. Further fractionations yielded a portion (b.p. 122.0–125.5°C. at 25 mm.), 12 per cent of the crude, which on repeated crystallization finally gave analytically pure $C_4H_2Cl_6$ (m.p. 9.5–11°C., b.p. 125.5°C. at 25 mm.), which would not add bromine and was not $CHCl_2CCl{=}CClCHCl_2$. From the still residues there was obtained some solid,

which on repeated crystallizations finally yielded analytically pure $C_4H_2Cl_6$ (m.p. 75–76°C.), which was probably not $CHCl_2CCl_2CCl_2CHCl_2$. Finally, $CCl_2{=}CCl_2$ and $CCl_2{=}CHCl$ were fluorinated in CF_3CCl_3 (Freon 113) solution at 0°C. In the first case, the results were similar to those given above, and in the second, only one analytically pure product was isolated, which was $C_4H_2F_2Cl_6$ (m.p. 55–56°C.).

The work which has just been described very briefly represents the first successful attempt to react elementary fluorine with pure liquid organic compounds containing more than one carbon atom. The contribution is definite, and the reactions, which take place under conditions favoring an atomic mechanism, will be discussed further in Section III. A study of this paper reveals throughout a degree of accuracy and precision which creates confidence in the results.

L. Patents

In addition to the work which has been detailed or referred to in the foregoing pages, a number of patents have been taken out in recent years, covering various processes involving direct fluorination. A number of these which have been abstracted will be summarized briefly below, but it should be understood that no exhaustive patent search has been attempted.

In 1934 the du Pont Company (98) patented abroad a process for fluorinating organic compounds in inert solvents, such as hydrogen fluoride, dichlorodifluoromethane, trichlorotrifluoroethane ($C_2F_3Cl_3$), and others, in the presence of catalysts such as iodine or antimony pentachloride. Benzotrifluoride, under these conditions, underwent polymerization. A year later I. G. Farbenindustrie (101) listed a procedure for carrying out such fluorinations in a chamber divided into small compartments by an inert packing such as calcium fluoride. Following this, Calcott and Benning (to du Pont) (94) and also Daudt and Parmelee (to du Pont) (96) took out American patents for direct fluorination in solvents, including many objects, conditions, and claims, but the procedures as described did not lead to the isolation of pure chemical individuals. Henne (to General Motors) (105) patented a process for reacting aliphatic halides containing halogens other than fluorine with elementary fluorine in the presence of pentavalent antimony compounds as catalysts. At least one halogen atom was replaced by fluorine, and the products separated in a dephlegmator. Calcott (to du Pont) (93) has also described a process for making a colored pigment by the direct fluorination of a copper phthalocyanine in liquid hydrogen fluoride. Finally, patents have been granted to I. G. Farbenindustrie (102, 103, 104) for a process involving the direct fluorination of oil- or wax-impregnated fibrous materials to be used for packaging or rubber for cell insulators; and to Gaylor (to Standard Oil Development) (99, 100) for a method of making fluorinated oils suitable for coating or impregnating wood and cloth, or as lubricating oils, antioxidants, and fireproofing agents. In the opinion of the writer, the procedures described in these patents are all characteristically indefinite, with the result that it is not possible to determine from the published reports to what extent they may lead to valuable developments.

This concludes the factual summary of the work in this field which has been published to the end of the year 1945.

M. Tabulation of fluorine compounds

Table 1 presents a list of fluorine compounds as prepared for the first time by direct fluorination.

III. THEORETICAL CONSIDERATIONS

The several investigators who have studied the action of elementary fluorine on organic compounds and whose work has been detailed in the foregoing pages have spent the greater part of their time and energies in developing experimental methods and accumulating data rather than in postulating and discussing reaction mechanisms. The reasons for this are not far to seek, since the field is new, the operating techniques difficult, and, until very recently, the literature background of necessity very scant. However, a number of theoretical discussions have been presented by some of the more recent investigators and these will be outlined in the same order as that used in the preceding section.

A. Contributions of Ruff

Ruff and Bretschneider (71, 74), it will be recalled, have shown that graphite or Norite will react with fluorine below the ignition point to form a very interesting compound best represented by the formula $(CF)_x$. With the added collaboration of Ebert, they have postulated a detailed mechanism for the formation of this substance, which was considered to be in substantial accord with the physical and chemical properties of the compound. The essentials of this theory are as follows: The fluorine molecules, first attracted to the carbon surface by van der Waals forces, next penetrate into the graphite lattice between the base planes of carbon rings of which it is composed. As a result, the distance between the planes is expanded from 3.4 A. to 8.17 A. and the fluorine molecules are changed to ions, presumably by acquiring electrons from the carbon rings. Then these ions, with a radius of 1.33 A., are packed in the most efficient possible manner into the volume provided by the expanded lattice, which, according to these investigators, requires them to lie in an orderly pattern in no less than six parallel planes, intermediate between the carbon base planes. The arrangement also necessitates that alternate carbon base planes be slightly distorted, by the displacement of certain carbon atoms in opposite directions. It was found that the volume necessary to pack in one fluoride ion per carbon atom in this manner required a lattice expansion which in turn corresponded very closely to the observed drop in density during the fluorination process. Also, the loss of electrons by the carbon rings to the fluorine should break up the conjugated systems in these rings, and so destroy the electrical conductivity of the graphite, which was found to be the case. Further, this arrangement assumes that while the distance between the carbon base planes is greatly increased, the ring structure within these planes is not greatly altered, and these assumptions were well supported by the observed x-ray data. Finally, if such a structure were rapidly

TABLE 1

Fluorine compounds as prepared for the first time by direct fluorination, either in analytically pure condition or otherwise adequately characterized

COMPOUND	MELTING POINT	BOILING POINT	INVESTIGATOR	REFERENCE	REMARKS
	°C.	°C.			
CH_3F		−78	Bigelow	(40)	
CH_2F_2		−52	Bigelow	(40)	
CHF_3		−82	Bigelow	(40)	
CF_4	−186	−130	Lebeau and Damiens	(53, 54)	
			Ruff	(76)	
$CFCl_3$	−111	24.1	Ruff	(77)	
CF_2Cl_2	−160	−28	Ruff	(77)	
CF_3Cl	−181	−80	Ruff	(77)	
CF_3NO	−150?	−84	Ruff	(80)	Mixed with $FCONF_2$
$FCONF_2$	−152.5	−82.4	Ruff	(80)	
CHF_2CH_2F	−84	3	Bigelow	(92)	
CHF_2CHF_2		−23.5 to −22.5	Bigelow	(92)	
CF_3CHF_2	−103	−48.5	Bigelow	(92)	
C_2F_6	−101	−78	Bigelow	(20, 73)	Originally prepared indirectly by Ruff (73)
CHF_2CH_2Cl		35	Bigelow	(22)	
$CHCl_2CFCl_2$		115.7	Miller	(58)	
CCl_3CFCl_2	100		Bockemüller	(10)	
$CFCl_2CFCl_2$	26.5	91	Bockemüller	(10, 44)	Highest purity: m.p. 28.1°C., b.p. 91.5°C.
CF_3CF_2Cl	−106	−38	Bigelow	(22)	
$(COF)_2$		26	Bigelow	(36)	
$(CNF_3)_2$	−128	−40	Ruff	(79)	Mixture of at least five isomers
C_3F_8	−183	−38	Simons	(87)	
CH_2FCOCH_3		78	Bigelow	(36)	
CF_3COCF_3	−129	−28	Bigelow	(36)	
C_4F_{10}			Simons	(87)	Reported properties conflicting (see text above)
			Bigelow	(37)	

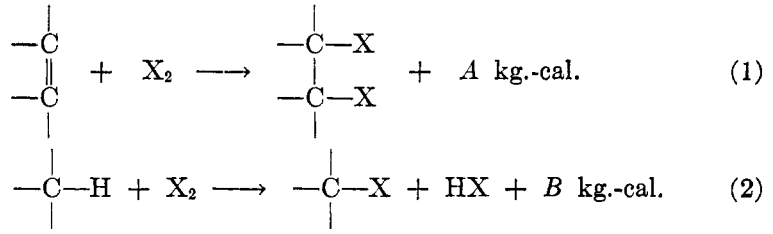
$C_4H_2F_2Cl_6$	55–56		Miller	(58)	
$CFCl_2CCl_2CCl_2CFCl_2$	4–5	152.5 (20 mm.)	Miller	(58)	Dimer
$C_4F_2Cl_8$		139–142 (13 mm.)	Bockemüller	(10)	Probably $CFCl_2CCl_2$-CCl_2CFCl_2 (?)
n-C_3H_6FCOOH		80–98 (13 mm.)	Bockemüller	(10)	Mixture of beta and gamma isomers
$CH_2FCHCOOH$ (with CH_3 on the CH carbon)		80–82 (13 mm.)	Bockemüller	(10)	
$CH_3CHFCHFCOOH$	Liquid at 0	100–102? (13 mm.)	Bockemüller	(10)	Contaminated by solid stereoisomer
$CH_3CHFCHFCOOH$	81		Bockemüller	(10)	
C_5F_{10}	−12 (about)	23	Simons	(87)	
			Bigelow	(37)	
$C_6H_{11}F$		100	Bockemüller	(10)	
C_6HF_{11}		62	Bigelow	(37)	
C_6F_{12}	48–49	50	Bigelow	(37)	See also Simons (60) and text above
				(87)	
$C_6F_4Cl_6$	94–96		Bigelow	(6)	
$C_6F_6Cl_6$	113–114		Bigelow	(6)	
C_7F_{14}		80	Simons	(87)	
$C_{12}F_{22}$	19–21	90 (90 mm.)	Bigelow	(37)	
$CH_3(CH_2)_7CHFCHF(CH_2)_7COOH$	81		Bockemüller	(10)	
$CH_3(CH_2)_7CHFCHF(CH_2)_7COOH$	95		Bockemüller	(10)	
$CH_3(CH_2)_7CHFCHF(CH_2)_7COOH$	84–85		Bockemüller	(10)	
$(CF)_x$	Decomposes		Ruff	(74)	Mixture (?); composition closely approximate

heated, the increase in volume produced by the formation of carbon tetrafluoride within the expanded lattice would be expected to result in the explosive disruption of the material, a result which actually took place under such conditions. From all this it will be clear that the theoretical assumptions involved have considerable experimental support.

The writer has been privileged to discuss the speculations just outlined with Drs. P. M. Gross, F. London, and M. E. Hobbs of this Department, who have given material assistance which is hereby gratefully acknowledged. While there is no doubt that the experimental work on which the theory is based is thoroughly sound, none of us can agree with the proposed ionic nature of the lattice of $(CF)_x$. Fluoride ions are negatively charged, and if they were packed together in successive layers as proposed, the repulsive forces would exceed the cohesive forces, and the whole structure would fly apart and so could not exist. Dr. London has proposed another possible structure involving only covalent links, which would greatly reduce the repulsive forces. In this model, the fluorine atoms are arranged in an orderly pattern in two parallel planes, one above and the other below each carbon base plane. The fluorine atoms are so arranged that two of them, one above and the other below, are connected by covalences to each carbon ring, making use of the two available electrons possessed by each such ring due to its partially unsaturated character. If the normal carbon–fluorine distance of approximately 1.4 A. is assumed, this structure requires that the adjacent fluorine planes be separated by a distance of about 5 A., in order to account for the observed density value. At first glance this distance would seem to be excessive, but such an equilibrium may readily be explained in the following manner. The electronegative fluorine atoms, although not ionized, are in any case partially charged and the adjacent layers of these atoms would be subject to fairly strong electrostatic repulsive forces, which could be adequately counterbalanced by the available long-range van der Waals attractive forces only at relatively large distances. These partially charged fluorine atoms represent an intermediate state between ions whose charges would exert repulsive forces too great to be counterbalanced at such distances as would be compatible with the density of the compound, and neutral fluorine molecules, as in liquid fluorine, which are subject to little or no electrostatic repulsion, but are kept apart by short-range van der Waals repulsive forces only. Altogether, the proposed concept represents a stable structure, accounts well for the physical and chemical properties of the compound, and last, but not least, seems much more satisfying than the one postulated by Ruff and his collaborators.

B. Contributions of Bockemüller

Bockemüller (10) in his theoretical discussion has called attention to the fundamental energy relationships involved in organic fluorinations, and has shown how they may readily account for the powerful and even "catastrophic" reactions which have often been observed. For example, in the typical addition and substitution reactions



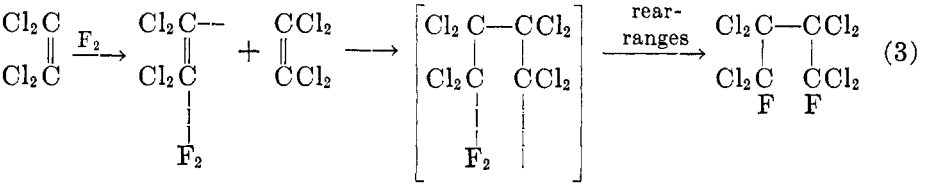
his values for A and B are approximately 107 and 103 when X = F, while they are only 33 and 23, respectively, when X = Cl. These heats of reaction are to be compared with the heat of formation (or disruption) of a C—C bond, which is about 71 kg.-cal. From the comparison it is obvious that the over-all heats of addition or substitution in the case of fluorine, unless adequately dissipated, are ample to disrupt an adjacent C—C linkage; furthermore, if the considerable heats of activation also set free at the moment of molecular or atomic impact are taken into consideration as well, the observed combustions, charring, and polymerizations may readily be explained.

It was on the basis of these considerations that Bockemüller decided to carry out fluorinations in dilute carbon tetrachloride solutions, in which the reacting molecules would be surrounded by layers of presumably inert solvent, and to use fluorine diluted with carbon dioxide, where the halogen itself was surrounded by inert gas molecules as well. These conditions, together with the relatively low temperatures maintained (0–15°C.), favored the rapid dissipation of the energy released by the reactions. On the other hand, since fluorine is but slightly soluble in carbon tetrachloride, the reactions must have taken place at the vapor–liquid interface, and furthermore, fluorine has been shown to react with carbon tetrachloride even at 0°C., at least in the presence of a chlorine acceptor (7), both of which factors would be disadvantageous. Nevertheless quite a number of saturated and unsaturated aliphatic compounds were fluorinated successfully by this method, as detailed in the preceding section, and this success was presumably due to relatively favorable rates of reaction prevailing under the specified operating conditions.

Among other things this investigator reported that the fluorination of butyric or isobutyric acid under the conditions just mentioned yielded either β- or γ-substitution products, but none of the corresponding α-derivatives. From this evidence, which was well supported, he drew the obvious conclusion that the mechanism of α-substitution must be different from that of β- and γ-substitution, but did not discuss the matter further. This interesting observation, once thought to be more or less incredible, fits in well with modern ideas, since Kharasch and Brown (47) have recently shown that when n-butyric acid or the corresponding acid chloride interacted with an *atomic* reagent, such as sulfuryl chloride, in the presence of benzoyl peroxide, β- and γ-substitution took place almost exclusively, whereas the usual catalyzed α-substitution is generally regarded as an *ionic* change. Thus it appears, perhaps for the first time, that direct fluorinations in the aliphatic series, even in dilute solutions, proceed to a

great extent at least by atomic chain mechanisms, a fact which has since been well substantiated, as will appear below.

It was also found that the direct fluorination of tetrachloroethylene (C_2Cl_4) yielded not only the expected $CFCl_2CFCl_2$, but also considerable $CFCl_2CCl_2$-CCl_2CFCl_2 and some CCl_3CFCl_2. The formation of the dimer was explained by assuming the interaction of an original, unstable addition product with a second molecule of C_2Cl_4 as follows:



(3)

and the presence of the pentachloro compound was accounted for by the simultaneous addition of fluorine and chlorine to the original substance. It was assumed, naturally, that the necessary chlorine had been set free by a simultaneous side reaction.

The entire change may readily be explained on the basis of the more modern atomic mechanism according to the scheme

$$F_2 \rightleftarrows 2F\cdot \quad \text{(thermal or catalytic)} \tag{4}$$

$$CCl_2{=}CCl_2 \xrightarrow{F\cdot} CFCl_2CCl_2\cdot \xrightarrow{F_2} CFCl_2CFCl_2 + F\cdot \tag{5}$$

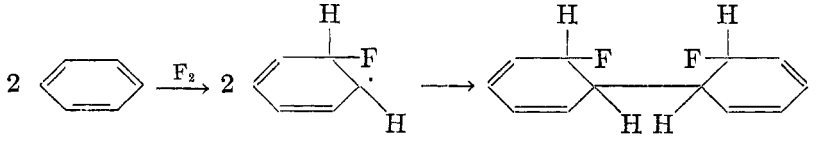
$$CFCl_2CCl_3 \xleftarrow{Cl\cdot} CFCl_2CCl_2\cdot \xrightarrow{\text{dimerization}} CFCl_2CCl_2CCl_2CFCl_2$$

the necessary chlorine atom having been set free by the reaction

$$RCl + F\cdot \rightarrow RF + Cl\cdot \tag{6}$$

This assumes, of course, that the chlorine atom collides with the excess of organic radical before either reacting with fluorine to form chlorine fluoride, or dimerizing to give molecular chlorine. Three other possibilities—namely, that either molecular fluorine or chlorine fluoride might have reacted directly with the halo-ölefin, or that the organic radical could have attacked chlorine molecules—are not necessarily excluded.

Finally, Bockemüller studied the fluorination of a number of aromatic compounds, and found that simple substitution did not take place, but that addition to the nucleus occurred instead and ultimately resulted in the formation of highly polymerized products containing fluorine, according to the scheme:



(7)

which could be repeated indefinitely. This formulation is essentially the same as the corresponding atomic mechanism, in which a fluorine atom would be repre-

sented as attacking a nuclear double bond, followed by dimerization of the resulting radical. Bockemüller then considered that if the unsaturated intermediates could be quickly saturated during the fluorination, the undesirable polymerization might be prevented, and definite products formed. Accordingly, he carried out the fluorination of benzoic acid in dilute carbon tetrachloride solution in the presence of a considerable concentration of bromine, which itself does not react appreciably with either the fluorine or the acid under these conditions. The resulting product contained practically no polymeric material, and finally yielded for the most part two portions having closely the compositions required by the formulas $C_6H_6F_4Br_2$ and $C_6H_6F_3Br_3$, which were thought to be derivatives of cyclohexane. This evidence, although not entirely conclusive, represents perhaps the first attempt to demonstrate experimentally the now well-recognized fact that the primary attack of elementary fluorine on the aromatic nucleus is one of addition by an atomic mechanism.

C. Contributions of Bigelow

The writer and his students have also been convinced for a long time that direct fluorinations take place, either in the vapor phase or in solution, by atomic chain mechanisms, and they have advanced a number of such postulations, as well as the more classical reactions, in order to explain the observed facts. Admittedly, these speculations lack rigid proof in all cases, but they have been put forward first, because they correlate and clarify most of the facts logically from a modern viewpoint, and further, since speculation, understood to be such, even if later disproved, is thought provoking and may lead to progress.

Young, Fukuhara, and Bigelow (92) fluorinated ethane in the vapor phase over a copper-gauze catalyst and obtained CF_4, C_2F_6, CH_3CHF_2, CHF_2CHF_2 and CHF_2CH_2F, but no mono- or difluoroethane. At this time they proposed the classical reactions to explain this, as follows:

$$C_2H_6 \xrightarrow{F_2} C_2H_5F \xrightarrow{-HF} CH_2{=}CH_2 \xrightarrow{F_2} CH_2FCH_2F \xrightarrow{-HF} CH_2{=}CHF \xrightarrow{F_2} CH_2FCHF_2 \quad (8)$$

followed by straight substitution and finally cleavage. This interpretation was based on the known instability of CH_3CH_2F and CH_2FCH_2F at elevated temperatures. This scheme, however, is not in line with the newer view that if the life of an intermediate is so short that the compound never exists in sufficient concentration to be isolated, it is better to assume that it is not formed at all, provided an adequate mechanism is available. If we postulate the formation of fluorine atoms first, according to equation 4 above, then we may write

$$CH_3CH_3 + F\cdot \rightarrow HF + CH_3CH_2\cdot \quad (9)$$

This radical should easily lose a hydrogen atom to fluorine

$$CH_3CH_2\cdot + F_2 \rightarrow HF + F\cdot + CH_2{=}CH_2 \quad (10)$$

followed by

$$CH_2{=}CH_2 + F\cdot \rightarrow \cdot CH_2CH_2F \tag{11}$$

or perhaps reactions 10 and 11, being practically simultaneous, could be combined to give

$$CH_3CH_2\cdot + F_2 \rightarrow HF + \cdot CH_2CH_2F \tag{12}$$

thus eliminating ethyl fluoride and ethylene from the picture. Then

$$\cdot CH_2CH_2F + F_2 \rightarrow HF + CH_2FCHF\cdot \tag{13}$$

similarly avoiding ethylene fluoride and vinyl fluoride. This last radical presumably would not be expected to lose a hydrogen atom to fluorine as readily as its predecessors, but rather to react in the more conventional manner:

$$CH_2FCHF\cdot + F_2 \rightarrow F\cdot + CH_2FCHF_2 \tag{14}$$

CH_2FCHF_2 was the least fluorinated molecule actually isolated. It should be noted here that in the series 9, 12, 13, and 14, only equation 9 requires active fluorine atoms, which are present in far lower concentrations than the corresponding molecules. The compound CH_2FCHF_2 contains the stable, resonating $\rangle CF_2$ group (15) and, once formed, would undoubtedly require an active atom for further fluorination; as these are in scarce supply, it accumulates in sufficient amount to be isolated. Then we have

$$CH_2FCHF_2 + F\cdot \rightarrow HF + \cdot CHFCHF_2 \tag{15}$$

$$\cdot CHFCHF_2 + F_2 \rightarrow F\cdot + CHF_2CHF_2 \tag{16}$$

and so on until hexafluoroethane is finally reached, and ultimately cleaved to carbon tetrafluoride. Naturally any such scheme, although it accounts for the observed results, cannot represent more than a part of the complex changes occurring in such a fluorination mixture. It also implies the formation of dimers and polymers from these radicals, which were not isolated; but their formation is by no means excluded, since the complex reaction product contained much material in transition fractions, residues, and the like, which could not be separated and identified.

Hadley and Bigelow (40) later fluorinated methane in a similar manner, and obtained not only the expected methyl fluoride, difluoromethane, fluoroform, and carbon tetrafluoride but also hexafluoroethane and octafluoropropane, thus demonstrating conclusively that a carbon chain may be built up as well as broken down by the action of elementary fluorine. All of these results may be explained very well by means of atomic mechanisms even simpler than those just outlined. For example, we have

$$CH_4 + F\cdot \rightarrow HF + CH_3\cdot \tag{17}$$

$$CH_3\cdot + F_2 \rightarrow F\cdot + CH_3F \tag{18}$$

and so on until carbon tetrafluoride is finally produced. However, when

$$CHF_3 + F\cdot \rightarrow HF + CF_3\cdot \tag{19}$$

the highly fluorinated radical does not react quite so readily with fluorine molecules, and so part of it dimerizes instead:

$$2CF_3\cdot \rightarrow C_2F_6 \tag{20}$$

Finally the following changes also appear to be reasonable:

$$CH_2F_2 + F\cdot \rightarrow HF + CHF_2\cdot \tag{21}$$

$$CF_3\cdot + CHF_2\cdot \rightarrow CF_3CHF_2 \tag{22}$$

$$CF_3CHF_2 + F\cdot \rightarrow HF + CF_3CF_2\cdot \tag{23}$$

$$CF_3\cdot + CF_3CF_2\cdot \rightarrow C_3F_8 \tag{24}$$

Although no higher polymers were isolated, these might well have been present in the highly complex product.

Continuing these studies, Fukuhara and Bigelow (36) turned to the fluorination of the volatile liquid acetone and finally obtained CH_2FCOCH_3, CF_3COCF_3, CF_3COF, $(COF)_2$, COF_2, and CF_4, together with other unidentified polyfluoroacetones and other products. Here it will be observed that fragmentation products instead of polymerization products have become important. However, the atomic mechanism seems quite adequate to account for all the known results in this instance also, as follows:

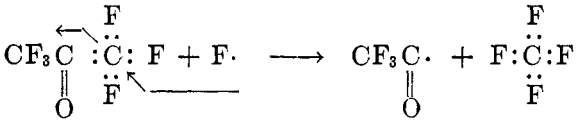
$$CH_3COCH_3 + F\cdot \rightarrow HF + CH_3COCH_2\cdot \tag{25}$$

$$CH_3COCH_2\cdot + F_2 \rightarrow F\cdot + CH_3COCH_2F \tag{26}$$

and so on until the completely fluorinated compound CF_3COCF_3 is reached. After that, we have

$$CF_3COCF_3 + F\cdot \rightarrow CF_3CO\cdot + CF_4 \tag{27}$$

or, more explicitly,



(28)

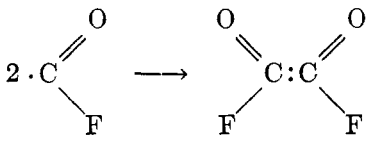
meaning that the unpaired electron on the fluorine atom enters the octet of a terminal carbon atom on the ketone, in order to form a pair. The resulting complex (see, for example, reference 16), of short life, then rapidly dissociates yielding the stable CF_4 and the $CF_3CO\cdot$ radical, thus completing the fragmentation of the carbon chain. Theoretically the fluorine atom could have attacked the ketone at several other points, but such reactions not only appear improbable, but also would lead to the formation of products which were not actually observed. The formation of the $CF_3CO\cdot$ radical moreover, accounts perfectly for all the other compounds isolated, as follows:

$$CF_3CO\cdot + F_2 \rightarrow F\cdot + CF_3COF \tag{29}$$

$$CF_3COF + F\cdot \rightarrow \cdot COF + CF_4 \tag{30}$$

Now the radical ·COF may either react with fluorine or dimerize:

$$\cdot COF + F_2 \longrightarrow F\cdot + COF_2 \tag{31}$$

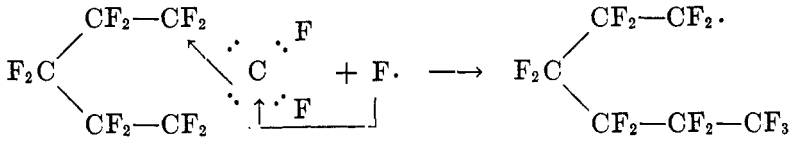


$$\text{or } (COF)_2 \tag{32}$$

It is of interest that Kharasch and coworkers (48) have found positive evidence for the existence of the analogous ·COCl radical. Finally, this mechanism would predict the formation of the dimer $CF_3COCOCF_3$, and while this compound was not isolated, definite evidence indicating its presence in the reaction product was reported.

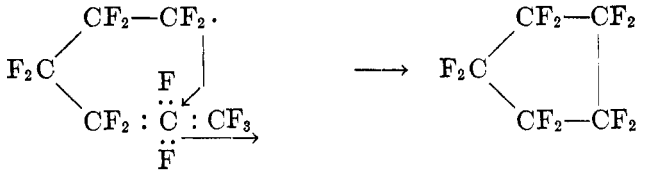
The next logical step in this series seemed to be the direct fluorination of benzene, and so Fukuhara and Bigelow (37) carried out this reaction, which proceeded easily and led to a clean but very complex product. Ultimately there were obtained C_6F_{12}, C_6HF_{11}, $C_{12}F_{22}$, C_5F_{10}, C_4F_{10}, C_3F_8, C_2F_6, and CF_4, but no aromatic substitution products whatever. These results indicate strongly that the reaction proceeded by an atomic mechanism involving, first addition, then substitution, and finally fragmentation, which may have been followed later by dimerization or polymerization of the fragments. There is no definite evidence to show that these processes do not go on simultaneously, but it seems more probable that they take place for the most part successively. No intermediates between benzene itself and C_6HF_{11} could be isolated under the operating conditions used, and need for further work in this important field is clearly indicated. However, any possible saturated intermediate of the $C_6H_6F_6$ type must have undergone direct substitution rather than thermal loss of hydrogen fluoride, since in the latter case aromatic fluorobenzenes should have been formed, but were not found.

In accord with the atomic mechanism already postulated, the formation of C_5F_{10} by fragmentation may be explained in the following manner:



(33)

followed by



(34)

and

$$2CF_3\cdot \longrightarrow C_2F_6 \tag{35}$$

This scheme represents the opening of the six-membered ring by an active fluorine atom (33), followed by the closing of the perhaps even more stable five-membered ring (34), through an attack by the unpaired electron on the octet of the spatially adjacent $>CF_2$ group with the simultaneous expulsion of a $\cdot CF_3$ radical from the molecule. Since the fluorine was always at relatively low concentration during the reaction, this hypothesis appears quite plausible and accords well with the observed fact that neither of the acyclic fluorocarbons C_6F_{14} or C_5F_{12} could be isolated from the products. It should be recognized here, however, that all such theories depend for their validity on the assumptions that the molecules in question were actually cyclic, and that they are really derivatives of cyclohexane and cyclopentane, respectively. These assumptions are certainly likely, especially since C_6F_{12} was the major product of the fluorination and neither fluorocarbon showed any signs of unsaturation, but they still lack rigid proof. One further indication that the C_6F_{12} had a symmetrical structure was its relatively high melting point, 48–49°C. Also, it is possible, though less likely, that C_5F_{10} could have been produced by polymerization of smaller fragments rather than by degradation of the larger molecules. All of the fluorocarbons of lower molecular weight which were obtained may readily be accounted for similarly, either by fragmentation or polymerization, or by both.

Finally, the formation of the interesting diphenyl derivative $C_{12}F_{22}$ may be explained without difficulty as a dimerization in the following manner:

$$C_6HF_{11} + F\cdot \rightarrow HF + C_6F_{11}\cdot \tag{36}$$

$$2C_6F_{11}\cdot \rightarrow C_{12}F_{22} \tag{37}$$

In the vapor phase, and in the absence of an excess of fluorine molecules or atoms' this relatively stable radical, which could not disproportionate easily, might well be expected to dimerize. Even if it were to attack a hydrocarbon molecule, the result would be the formation of C_6HF_{11}, and the process would then be repeated. Altogether, it appears that essentially all the known facts concerning this interesting and important fluorination may be correlated and clearly explained on the basis of an atomic mechanism.

D. Contributions of Miller

In concluding this brief theoretical survey, mention should be made of the recent interesting work by Miller (58), dealing with the direct fluorination of liquid organic halogen compounds. He considered that these reactions, which took place either at a vapor–liquid interface or in the gas phase (see above), proceeded essentially by atomic mechanisms, but did not outline any of them specifically in his published paper, which was devoted in the main to the presentation of precise experimental results. The present writer has therefore selected two of these liquid fluorinations as illustrations to show how well the atomic mechanism may be applied to correlate and explain the results obtained under these conditions.

Miller found that the fluorination of CCl_3CHCl_2 yielded, ultimately, in the order of their boiling points, $CFCl_2CFCl_2$, $CCl_2{=}CCl_2$, CCl_3CFCl_2, CCl_3CCl_3,

and $CCl_3CCl_2CCl_2CCl_3$. The formation of these compounds may be explained as follows:

$$CCl_3CHCl_2 + F\cdot \rightarrow HF + CCl_3CCl_2\cdot \quad (38)$$

$$CCl_3CCl_2\cdot + F_2 \rightarrow F\cdot + CCl_3CFCl_2 \quad (39)$$

$$CCl_3CCl_2\cdot + F_2 \rightarrow F\cdot + ClF + CCl_2{=}CCl_2 \quad (40)$$

$$2CCl_3CCl_2\cdot \rightarrow CCl_3CCl_2CCl_2CCl_3 \quad (41)$$

$$CCl_3CHCl_2 + ClF \rightarrow HF + CCl_3CCl_3 \quad (42)$$

$$CCl_2{=}CCl_2 + F_2 \rightarrow CFCl_2CFCl_2 \quad (43)$$

It is clear, of course, that such a complex mixture could be formed by many different routes, of which the above seem most logical since they require a minimum of the activated fluorine atoms, which are present at low concentrations. The compound chlorine fluoride is used as the chlorinating agent on account of the very high heat of formation of hydrogen fluoride, and a considerable concentration of this substance can easily result from the impact of fluorine atoms on any chlorinated molecule according to the scheme:

$$RCl + F\cdot \rightarrow ClF + R\cdot \quad (44)$$

It is not considered probable that significant concentrations of either molecular or atomic chlorine were present in the reaction mixture, although the latter could have been formed according to the equation

$$RCl + F\cdot \rightarrow RF + Cl\cdot \quad (45)$$

or even

$$R_2C{=}CR_2 + FCl \rightarrow R_2CFCR_2\cdot + Cl\cdot \quad (46)$$

and so make possible a certain amount of direct chlorination.

Miller also reported that the fluorination of $CHCl_2CHCl_2$ yielded $CFCl_2CFCl_2$, $CCl_2{=}CHCl$, $CHCl_2CFCl_2$, and CCl_3CHCl_2, but no C_2Cl_6. These results may be accounted for by the changes:

$$CHCl_2CHCl_2 + F\cdot \rightarrow HF + CHCl_2CCl_2\cdot \quad (47)$$

$$CHCl_2CCl_2\cdot + F_2 \rightarrow F\cdot + CHCl_2CFCl_2 \quad (48)$$

$$CHCl_2CCl_2\cdot + F_2 \rightarrow F\cdot + ClF + CHCl{=}CCl_2 \quad (49)$$

This implies that the residual hydrogen atom is well shielded by the large adjacent chlorine atoms. It is also quite possible that this last change is entirely thermal, and requires no fluorine, as

$$CHCl_2CCl_2\cdot \xrightarrow{\text{heat}} CHCl{=}CCl_2 + Cl\cdot \quad (50)$$

Then

$$CHCl_2CHCl_2 + ClF \rightarrow HF + CCl_3CHCl_2 \quad (51)$$

and

$$CHCl_2CFCl_2 + F\cdot \rightarrow HF + \cdot CCl_2CFCl_2 \quad (52)$$

$$\cdot CCl_2CFCl_2 + F_2 \rightarrow F\cdot + CFCl_2CFCl_2 \quad (53)$$

The other reactions studied by Miller may in most cases be explained without difficulty in a similar manner.

Theoretical speculations like those outlined in the greater portion of this section undoubtedly possess numerous shortcomings. On the one hand, there are many things, such as the properties of the aromatic nucleus, which an electronic formula cannot fully portray; while on the other, it has been alleged, not without point, that with a little mental dexterity such mechanisms can be made to account for every observed reaction, and for many more which are not observed. All this has its roots in the fact that the symbols we use only very roughly represent the entities for which they are supposed to stand. However, as has been said before, these theories, when labelled as such, are well worth while provided they first correlate and explain, next stimulate thought, argument, and disagreement, and finally lead to experiment and progress.

IV. FLUORINE GENERATORS

Since elementary fluorine has not yet been made available commercially[2] and in the past has almost invariably been produced as used, it would appear to be desirable to introduce here a discussion of fluorine generators. However, this field is in itself so extensive that no more than a representative survey can reasonably be attempted.

Fluorine has almost always been prepared by the electrolysis of alkali metal fluorides, mostly potassium bifluoride, KHF_2, either molten or dissolved in anhydrous hydrogen fluoride at various concentrations. Since Moissan's time about a score of generators have been described, operating under widely differing conditions and yielding, as might be expected, quite different results. While in general the procedure is not really difficult to carry out, it is safe to say that in each individual case notable obstacles have been encountered, and that the ideal apparatus probably has yet to be described. For our present purpose, five generators, representative of the more important types, will be considered in some detail here. An effort will be made to point out the respective advantages and limitations of the different units, the problems which have in general been encountered, and, in the writer's opinion, what would seem to be the direction of progress.

[2] Note, however, the statement by Wartenberg (90a) regarding the loan to him for experimental purposes of a cylinder of fluorine (75 per cent fluorine, 17 per cent nitrogen, 8 per cent oxygen by volume) from the I. G. Farbenindustrie A.-G.

A. The Moissan generator

The first successful fluorine generator was, of course, the one described originally by Moissan (62, 63). He isolated the element for the first time by the electrolysis of an approximately 30 per cent solution of potassium bifluoride in anhydrous hydrogen fluoride maintained at a temperature between −23° and −50°C. in order to prevent volatilization of the solvent. The apparatus, which was made entirely of platinum, consisted essentially of a U-tube with side-arm delivery tubes, equipped with tight fluorite stoppers carrying the electrodes, and surrounded by a bath of liquid methyl chloride. The anode, at which the fluorine was liberated, was made of a highly resistant platinum–iridium alloy, but even this was seriously corroded. The anhydrous hydrogen fluoride required for the electrolyte was prepared by heating pure potassium bifluoride in a platinum retort, the salt having previously been desiccated with great care under reduced pressure. Every precaution seems to have been taken to exclude air and moisture during this operation and also the subsequent electrolysis. The fluorine was evolved at the rate of 1.5–2.0 liters per hour, using a current of 3.5–4.5 amp. at a potential drop of about 40 volts, but data regarding the current efficiency of the cell do not appear to have been given.

There would seem to be little doubt that the anode gas consisted of elementary fluorine in a relatively high state of purity, since it readily ignited crystalline silicon and, after being freed from entrained hydrogen fluoride, was absorbed completely by metallic mercury in the cold, as well as by heated iron contained in a platinum tube. In the latter case, the increase in weight of the iron presumed to be due to fluorine was shown to be closely equivalent to that of the hydrogen liberated at the cathode during the same period. The mercury-absorption test would seem to exclude the possibility that the anode gas contained oxygen, and perhaps oxygen fluoride as well; but the reaction with heated iron would certainly not do so, since these impurities would be absorbed readily at the same time. Had this occurred, then the fluorine actually produced would have been definitely less than equivalent to the corresponding cathode hydrogen, a result which would naturally be anticipated on account of the corrosion of the anode during the electrolysis. Many years later Ruff (72) studied the Moissan generator intensively, and found that under the best conditions the electrical efficiency with respect to fluorine was only 30 per cent, while that with respect to hydrogen was only 40 per cent, thus lending support to Moissan's observation that they were not far from the same. These very low values were found to be due to (*1*) the reaction of fluorine with the platinum anode, (*2*) the reaction of hydrogen with platinum compounds progressively dissolved by the bath, (*3*) the simultaneous liberation of some hydrogen and some fluorine in the anode and cathode chambers, respectively, and (*4*) the presence of water in the electrolyte. All of these considerations taken together leave a slight uncertainty as to the exact quantitative composition of the fluorine gas originally obtained when the element was discovered.

Some years later, Moissan (67) described a similar generator using a copper

U-tube, and giving approximately the same results more economically. He found, however, that a copper anode could not be used successfully, since a film of metal halide caused polarization.

Moissan's pioneer generator stands as the classical example of the U- or V-type cells, and of the use of a metallic anode in the production of fluorine by electrolysis. It also operated at very low temperatures with a relatively dilute but presumably anhydrous electrolyte. It had the fundamental asset of being highly successful for the purpose for which it was intended, but also possessed a number of significant disadvantages. The initial cost was very high, the expensive anode was attacked by the fluorine, the procedure, including the preparation of the anhydrous hydrogen fluoride, required highly skilled operators, and the apparatus as well as the process as described could not easily be adapted to production on a larger scale without much modification. In the decades immediately following, these practical obstacles operated to deter scientists from preparing and studying the new element, in spite of the excellence of the original work.

B. The Mathers generator

In 1919 Argo, Mathers, Humiston, and Anderson (3) described a new generator which, at the outset, gave promise of obviating most of the difficulties encountered by Moissan and has since become generally known as the Mathers generator. In this case, the fluorine was produced by the electrolysis of molten potassium bifluoride, at temperatures from 250–300°C. The apparatus consisted essentially of an electrically heated cylindrical vessel, made of heavy copper and open to the air, which contained the electrolyte and also served as the cathode. The anode was made of a thick graphite rod, suspended in the melt by means of a copper bolt, and completely surrounded by a cylindrical copper diaphragm, closed at the top, and provided with an exit tube for the fluorine as well as a series of slots near the bottom to facilitate the electrolysis. The rod which carried the anode passed directly through an insulating stuffing box filled with powdered fluorspar, which was supported on a fluorite ring and compressed by a jam nut. The diaphragm was also equipped with a removable plate at the bottom, in order to prevent any hydrogen rising from below from entering the anode chamber and reacting explosively with the fluorine.

The electrolyte was prepared by treating potassium fluoride with an excess of commercial hydrofluoric acid, and always contained water at the start. The mixture was slowly heated in an open metal container for several hours, until the temperature reached 225°C., to expel the excess of water and acid. Then the melt was transferred to the cell, where it was electrolyzed for several additional hours at a low current density in order to remove the remainder of the water; it was not considered to be very hygroscopic after being dehydrated in this manner. This preliminary electrolysis was necessary in order to avoid almost complete polarization of the cell due to the formation of an oxygen gas film on the surface of the anode. Afterwards, at a temperature of about 240°C., fluorine was evolved freely and the generator could be operated continuously at a much

higher current density without polarization. The exhausted bath could not, according to the published report, be regenerated by passing hydrogen fluoride into it. Instead, it was poured out, frozen, ground, and redissolved in hydrofluoric acid, after which the heating and dehydration were repeated. In operation under favorable conditions at 225–250°C., using a current of 10 amp. at a potential drop of 12–15 volts, fluorine was evolved at a current efficiency stated to be about 70 per cent. No comment seems to have been made regarding the analytical composition of the anode gas, beyond the general implication that it consisted of nearly pure fluorine.

The writer and his students used a generator (7) of the Mathers type for a period of several years, and so can speak from experience regarding it. The advantages of this unit were clearly obvious even to the more casual observer. It was rugged in construction and relatively inexpensive, the anode was cheap and but little attacked, the procedure did not require the services of very highly skilled operators, and the apparatus could easily be adapted to larger-scale production. Unfortunately, however, this type of generator has a number of serious limitations, some of which, at least, were probably not fully realized by the original investigators, who were engaged in an effort to produce toxic gases under the pressure of wartime conditions.

Most important of all, much recent experience has made it clear that (*a*) the electrolysis of the bath at low current density, using less than 10 amp. even for the entire life of the charge, would not dehydrate it completely; (*b*) the electrolyte was markedly hygroscopic, especially on standing exposed to the air; and (*c*) unless the melt was completely anhydrous, the anode gas contained large and widely varying quantities of oxygen and oxygen fluoride. This remained true to a considerable extent even when the melt was sufficiently dry to undergo electrolysis smoothly and without polarization. These facts have been well substantiated by numerous analyses of the anode gas prepared in this Laboratory by Day (24) and by Miller (59), who has also collected and discussed a considerable body of evidence from the literature in regard to the contamination of fluorine obtained in this manner. It has even been found that high atmospheric humidity had an adverse effect upon the composition of the anode gas. While it is probable that a further electrolysis of this kind of melt at higher current densities, using more than 10 amp., would ultimately dehydrate it before the exhaustion of the charge, it certainly would not remain anhydrous for any considerable time if left standing exposed to the air, either heated or frozen. Incidentally, it has been found entirely practicable to regenerate an exhausted charge by passing anhydrous hydrogen fluoride into it, contrary to the earlier report (3). It should also be clear that the limitations just outlined would apply not only to the Mathers type of generator, but to all units in which strictly anhydrous conditions cannot be or are not maintained.

This type of generator also possesses several lesser, but still very real, drawbacks. In the writer's experience, on account of the high temperature a considerable amount of copper was dissolved, transported, deposited, or precipitated. This was found to result in much corrosion of the diaphragm, with attendant

contamination of the electrolyte and the accumulation of sludge. During the operation of the cell, detonations, sometimes powerful, occurred from time to time in spite of much care. They were probably due to the recombination of hydrogen and fluorine, and usually took place in the cathode compartment, when fluorine bubbled into it through the diaphragm, presumably owing to the obstruction of the exit tube by frothing viscous electrolyte. Under these conditions the explosions were essentially harmless, but at rare intervals and for reasons not well understood, they took place in the anode compartment; this resulted in the forcible expulsion of molten electrolyte from the cell and in this case constituted a real hazard. Perhaps it should also be mentioned that the fluorite ring was very fragile, salt bridges in the anode chamber at times caused annoying short circuits, and recurring polarization was frequently time-consuming.

There can be no doubt that the Mathers generator represents a real advance along the difficult way toward fluorine production. Nevertheless, from the preceding outline it will be clear that neither this unit, nor similar ones which have followed it, when operated intermittently, open to the free access of air and moisture as described, can be relied upon to produce consistently either analytically pure fluorine or an anode gas of constant composition.

C. The Fredenhagen generator

About a decade later, in 1929, Fredenhagen and Krefft (34) described another generator, identical in principle with the Mathers unit but differing from it in several important respects, in that moisture was rigorously excluded, and an anhydrous electrolyte employed, which was repeatedly regenerated by means of anhydrous hydrogen fluoride. The electrically heated, cylindrical, copper electrolysis vessel serving as the cathode was provided with a thick cover of the same metal, which fitted tightly into a top flange by means of a polished and tapered joint. The insulated graphite anode, supported on a nickel rod, was surrounded by the usual perforated copper diaphragm, also insulated, and equipped with a hydrogen baffle at the bottom. The nature of the insulating material was not given.

The potassium bifluoride electrolyte was presumably dehydrated in the apparatus itself by a patented process (106), which consisted essentially in passing dry air through the crystalline solid salt at elevated temperatures and reduced pressure for such time that when the bifluoride was subsequently heated to a high temperature, the hydrogen fluoride evolved showed a minimum electrical conductivity. This procedure would be expected to yield a very dry charge, which was regenerated without difficulty after electrolysis by bubbling anhydrous hydrogen fluoride, made by heating dry potassium bifluoride (32), directly through it. The electrolysis was conducted over a slowly rising temperature range from 160–250°C., corresponding to a progressive change in the composition of the electrolyte by the loss of hydrogen and fluorine from $KF \cdot 1.6HF$ to $KF \cdot 0.8HF$, when it was regenerated. The fluorine was given off smoothly, using an average current of 20 amp. at a potential drop of 8.5–9 volts, at the rate

of 7.6 liters per hour and a current efficiency of 92–94 per cent. The product was considered to be free from oxygen and other contaminants, but no analyses were given, and the method by which the very high efficiency was measured was not indicated.

These investigators have found that when the proportion of hydrogen fluoride in the melt was greater than that corresponding to KF·1.8HF, the graphite began to be wet by the electrolyte and soon disintegrated mechanically, whereas if the proportion was less than that corresponding to KF·0.8HF, the internal resistance of the bath was greatly increased. In the intermediate working range, however, the graphite was neither attacked nor wet by the electrolyte, and showed a constant overvoltage of 5 volts, presumably due to the presence of a very thin film of vapor at the anode surface. They also reported that the melt absorbed water greedily from the air even at 250°C., and they made some interesting observations concerning the effect of water on the process. When the melt contained more than 1 per cent, or less than about 0.3 per cent, of water, the electrolysis proceeded smoothly, yielding oxygen in the former case and essentially fluorine in the latter. In the intermediate range however, erratic and troublesome polarization occurred, due to the overspreading of the graphite by an insulating oxygen gas film. This led to potential drops up to 50 volts, accompanied by sparking through the gas film and injury to the electrode. These observations emphasize the great importance of and even necessity for the use of a strictly anhydrous electrolyte.

The Fredenhagen generator and procedure would seem to avoid the major difficulties involved in the Mathers method, since an essentially dry electrolyte was maintained anhydrous in a closed apparatus and regenerated by dry hydrogen fluoride. Unfortunately, however, no analyses of the anode gas were presented to support the claim that it was practically pure fluorine, presumably after the removal of hydrogen fluoride. The product may have been free from oxygen compounds, but undoubtedly it contained a small but unknown amount of carbon fluoride, according to earlier reports. No definite comment was made concerning anode or cathode chamber explosions, salt bridges or entrainment, and the disintegration of insulating material. It would be interesting to know if any of these difficulties were actually encountered, and if so, how they were met. These investigators have made a distinct contribution by setting forth clearly the serious and varied effects of progressively changing proportions of water in the electrolyte, and have supported these statements with a considerable body of experimental data. In addition, they have reported the range of hydrogen fluoride concentration in the melt in which a graphite anode could practicably be used. Altogether the methods and results as presented are satisfying, and in considerable measure convincing.

D. The Cady generator

The next generator to be considered was described recently by Cady (18), and was essentially different from the others in that it operated at a medium temperature of 75°C. and had a nickel anode. No particular effort was made

in this case to exclude moisture rigorously during the process. The gas-heated, cylindrical reaction vessel, serving as the cathode, was made of Monel metal, provided with a flat flange at its upper edge and covered by a sheet-copper lid. A cylindrical copper diaphragm, closed at the top, which also served as anode support, electrical conductor, and hydrogen fluoride bubbler, was suspended from the lid by a copper tube, which passed through an insulating stuffing box filled with Portland cement. This tube was used to conduct the fluorine from the apparatus, and was also connected to the positive pole of the D.C. circuit. Four large square holes were cut in the diaphragm near its lower end, which itself was closed by a copper plate carrying the anode. The latter was made from a roll of thin sheet nickel, which was bolted to the inside surface of the plate and projected for a short distance upwards.

The electrolyte was prepared by melting a charge of technical potassium bifluoride in the cathode receptacle, at a temperature somewhat below 250°C., and subjecting the melt to a preliminary electrolysis, using a graphite anode and a current of 12–15 amp., until such time as fluorine was liberated. This required not more than 3 hr., during which time the polarization and arcing at the anode were periodically relieved by opening the circuit. Then anhydrous hydrogen fluoride was passed directly into the melt, in such a manner that the latter was always maintained at a temperature not far above its melting point, and the process was continued until the melt contained about 43.4 per cent hydrogen fluoride, corresponding fairly closely to the composition required by the formula $KF \cdot 2HF$. This procedure, which was necessary in order to avoid undue loss of hydrogen fluoride, required a progressive lowering of the temperature of the melt from 250°C. to a little above 70°C. Then, with the diaphragm in place and the lid slightly raised to avoid explosions in the cathode chamber, the cell was ready to operate. During the electrolysis, the copper diaphragm became coated with an insulating layer, and the anode gas was liberated only from the nickel. At a temperature of 73–75°C., using a current of 12 amp. at a potential drop not stated for this unit (but probably about 10 volts (19)), fluorine was produced at an average current efficiency of 72 per cent. A sample of the product contained in a glass bulb was found to be absorbed by metallic mercury to the extent of 98 per cent, but neither the conditions of sampling nor other details of this analysis were given. Interestingly enough it was observed that an electrolyzing current of 8 amp. produced sufficient heat to maintain the generator at 75°C. For lower or higher currents it was necessary to heat or cool the cell, respectively, in order to maintain the required temperature. The electrolyte was considered to be exhausted when it would no longer remain completely liquid at 75°C., and it was regenerated by bubbling anhydrous hydrogen fluoride into it through the diaphragm, until it again contained about 43.4 per cent of hydrogen fluoride. The addition was presumably controlled by titration, but this is not so stated. Cady (19) subsequently described a somewhat improved generator of the same type, which was steam heated and had an anode suspension similar to Fredenhagen's, but its performance was essentially the same as that of the apparatus just considered.

These generators, which were intentionally patterned after an older model by Lebeau and Damiens (52), were almost certainly an outgrowth of an earlier work by Cady (17), in which he presented the freezing point–composition diagram for the system KF·HF, together with related vapor pressures. In this paper he has made clear quite convincingly that, on theoretical grounds at least, there are three temperature ranges within which the electrolysis would be practicable. These lie in the vicinity of −80°, 70°, and 240°C., respectively, and represent conditions such that a considerable variation in the composition of the liquid does not affect the melting point too greatly, and also such that the corresponding vapor pressures are relatively low.

In addition to high-temperature generators, the writer has had several years' experience (8) with a medium-temperature unit using a nickel anode, which was very similar to Cady's in principle but differed from it somewhat in detail. The advantages of this type of outfit were not far to seek. First, it operated under conditions under which the melting point of the bath was least affected by changes in its composition. Then, the medium temperature employed markedly reduced corrosion, as well as heating costs and operating difficulties. Finally, the use of the nickel anode completely avoided the troublesome polarization phenomena associated with graphite, and at the same time made certain that the product could not be contaminated with volatile carbon fluorides.

On the face of it, such advantages would appear to be compelling, but unfortunately this type of cell too has inherent limitations which must be both recognized and successfully met, if satisfactory performance is to be expected. First of all, and most important, the usual smooth operation of this kind of generator, in the complete absence of polarization effects, gives no outward indication whatever of the actual composition of the anode gas, which can vary over a wide range. Without adequate analytical control, this fact alone has frequently led to disappointment and loss. We have found (8), for example, that when a generator of this general type, operating in routine fashion for many hours at 5 amp., was taken from the line and tested, the anode gas after the removal of hydrogen fluoride was found to contain only 75.5 per cent of fluorine by analysis, using the apparatus to be described in the following section. Also, a special test generator operated for a long period failed to yield good fluorine at all when a current of 5 amp. was used, but with 10 amp. or more, the melt was dehydrated in 2–3 hr., after which the anode gas contained essentially 100 per cent fluorine by analysis. Furthermore, when the same test generator, with the melt anhydrous, was tightly closed and allowed to stand hot overnight, on resumption of the electrolysis, using 5 amp., the anode gas, after 30 min., contained only fluorine. However, if the melt was allowed to stand exposed to the air, even if only to the extent of two small portholes in the cell cover, the results were quite different. Under otherwise identical conditions, on resumption of the electrolysis after standing over one night, the anode gas contained only 83 per cent of fluorine, and after standing over 48 hr., it contained only 53 per cent of the halogen by analysis. These figures would apply, of course, not only to the units under discussion, but also in equal measure to all open-type generators.

Another difficult problem encountered with the Cady-type unit was that of corrosion of the anode, accompanied by serious contamination of the electrolyte and low current efficiency. These effects have been found to be somewhat dependent upon the temperature, which had to be maintained as low as possible. To accomplish this, however, would require a careful control at all times of the concentration of hydrogen fluoride in the electrolyte within a narrow range, since too little would cause the bath to freeze, while too much would result in serious contamination of the anode gas by hydrogen fluoride. In our experience, under somewhat different conditions, the corrosion was heavy and accompanied by current efficiencies as low as 35 per cent. Also, the progressive contamination of the electrolyte, with attendant increase in viscosity, seemed to contribute to the production of powerful anode-chamber explosions which were observed from time to time. It is recognized of course that these results of ours were not necessarily strictly comparable to those to be obtained from the exact Cady model and conditions, but they have seemed sufficiently definite and analogous to be worthy of mention.

From the accumulated evidence it is clear that, while Cady's generator can produce good fluorine, there is no certainty that it will do so, especially when operated intermittently, unless moisture is effectively excluded from the anhydrous electrolyte at all times. The only exception to this would be when the unit is in actual operation using a current of 10 amp. or more, which, according to our experience, is sufficient to dehydrate the electrolyte in an open generator. Furthermore, it appears likely that the necessary continuous control of the composition of the bath within a narrow range would be time-consuming; and finally, a serious loss of nickel and consequent contamination of the melt can hardly be avoided. These considerations, it would seem, have not received sufficient emphasis in the published reports.

E. The Miller and Bigelow generator

The last generator to be considered in detail here was described by Miller and Bigelow (60), and was designed to produce essentially pure fluorine consistently by the simple expedient of operating throughout under strictly anhydrous conditions. The fluorine was generated by the electrolysis of dry potassium bifluoride in the high-temperature range, using graphite electrodes. The apparatus consisted of a heavy, cast-nickel, U-shaped vessel, provided with polished flanges at the ends, and equipped with polished cast-nickel caps, made gas-tight by lead gaskets and held firmly in place by parallel steel plates which were tightly compressed by steel bolts. The two graphite electrodes were screwed to nickel rods, which passed directly through the caps, and were held rigidly suspended by means of a resistant insulating packing made from powdered fluorspar and Portland cement. The caps were also provided with drilled holes, equipped with adequate couplings, for the escape of the fluorine and hydrogen, respectively, and a thermometer well extended directly into the main casting. The entire unit was contained in a rectangular box-shaped electric heater, so arranged that the caps were kept hot enough to melt any of the electrolyte which was entrained. The pure crystalline bifluoride was completely dehydrated

in a tightly closed, vertical metal tower, which was electrically heated and provided with a thermometer well at the top and a large spout at the bottom. At first dry air (106) was passed through the charge at 150°C. under reduced pressure, and this was later displaced by fluorine gas (41) to complete the dehydration effectively, when fluorine of the highest quality was desired. Then the electrolyte was melted by raising the temperature, and finally run rapidly through the spout into the generator with the minimum possible exposure to air and moisture. In operation at 250–300°C., using a current of 5 amp. at a potential drop of 18–20 volts, this unit functioned very smoothly and produced fluorine which was 94.4–99.0 per cent (±0.1 per cent) pure by analysis, at the rate of about 2 liters per hour and a current efficiency of 61–89 per cent (±2.5 per cent), depending on the age of the charge and the efficacy of the drying. The apparatus would run about 25 hr. before the charge was exhausted and had to be replaced. Later on it was found that the electrolyte could easily be regenerated with anhydrous hydrogen fluoride, even at high temperatures, and thus it was possible to continue up to nearly 100 hr. before recharging and reconditioning finally became necessary.

The most important advantage of this generator was that it eliminated completely the contamination of the anode gas by unknown and widely variable proportions of oxygen and oxygen fluoride, and yielded consistently reproducible results, as stated above. In addition it was rugged, could be adapted reasonably well to large-scale production, was almost unaffected by corrosion on account of a protective surface coating on the nickel, and operated for long periods of time with great smoothness and no trace of violent reactions of any kind. The electrolyte was scarcely contaminated by nickel salts, and neither electrode was seriously attacked after many hours in service.

It would be a pleasure to record that this particular generator had no significant limitations, but, unfortunately, as in all the other cases discussed, such was not the fact. Perhaps the greatest difficulty encountered in its use was the tendency of less skilled operators to cut short the rather tedious dehydration process, which could not be completed within the cell itself because the maximum current capacity of about 10 amp. was too low. Under these conditions all the polarization phenomena so well described by Fredenhagen and Krefft (34) came into play, resulting in serious loss of time and possible disintegration of the electrodes, not to mention an impure product. Other difficulties were the infiltration of the electrolyte between the nickel and the graphite, causing the electrodes to crack at times, and the formation of salt bridges over the insulating packing, resulting in the partial or complete short circuit of the electrolyte and the rapid corrosion of the nickel rods at these points. Also, the actual capacity of the unit was low, while the manipulation of a relatively heavy metal unit at high temperatures was noticeably laborious. Finally, it was possible for an obstruction in the fluorine line to cause the eventual clogging of both exit tubes from the generator with frozen melt, resulting in the building up of high pressures within the tightly closed unit. This real hazard was completely overcome, however, by the use of a hydrogen flowmeter and indicator at all times. Alto-

gether, the closed unit can be depended upon to produce fluorine of very high purity consistently and efficiently provided it is skillfully operated, but it now appears possible that the necessary maintainance of a strictly anhydrous electrolyte may well be accomplished in a somewhat simpler fashion.

F. Generalizations and tabulation of generators

In concluding this section it is hoped that the foregoing somewhat detailed description and discussion of five typical units may be considered sufficiently representative to serve as a basis for such generalizations as may be made concerning laboratory fluorine generators. There are five main topics to be considered: namely, (*a*) type of unit, (*b*) operating temperature range, (*c*) anode material, (*d*) condition and regeneration of the electrolyte, and (*e*) miscellaneous items.

In the light of our present experience, of these topics only *d* may be considered to be finally settled. There is no longer any doubt that while the evolution of fluorine is proceeding, either (*1*) the electrolyte must be completely anhydrous or (*2*) the anode gas will contain presumably considerable, and certainly unpredictable, quantities of oxygen and oxygen fluoride which are difficult to remove. The bath may be rendered anhydrous by a preliminary electrolysis for several hours when using a current of more than 10 amp. but can be maintained so *only* by using a tightly closed unit. The sole exception to this is when the respective exit gases are issuing from the apparatus at rates sufficient to counterbalance completely the diffusion of moisture in the opposite direction. The regeneration of the melt by passing commercial anhydrous hydrogen fluoride directly into it is now a universally accepted procedure, but care must be taken that the gas is really anhydrous, or much trouble may result. Also, the quantity added should be controlled carefully, either (*1*) by the addition of known amounts (weighed or measured) or (*2*) by the semiquantitative testing of the electrolyte itself.

With regard to the other topics, where final decisions cannot yet be made, it becomes necessary to apply individual judgment. It is more than probable that most of the generators which have been described can be made to yield good fluorine, provided the intelligent operator is sufficiently convinced of the value of his outfit to make the necessary adjustments, compensations, and effort. Without these, however, the results might well be very different.

Of all the different types of units which have been used, it seems likely that the diaphragm type, employing an electrically heated cylindrical container, is the most adequate, since it is compact, easy to handle, and has the greatest relative capacity for the electrolyte. It may be made of copper, nickel, Monel metal, or even steel (18), but it must be tightly closed, either by clamps with a safety tube, as suggested by Bockemüller (10), or even better by polished tapered joints, according to Fredenhagen (34). The container should not act as the cathode (10), so that the diaphragm may be open at the bottom and perhaps abbreviated in length without incurring the risk of mixing hydrogen with fluorine. In this case, however, the area of the insulated metal sheet, or perhaps cylinder,

serving as the cathode must be sufficiently great to avoid the occurrence of annoying overvoltages (19) at this point. Finally, in any larger unit metal condensers should be provided, and arranged so as to return volatilized hydrogen fluoride to the melt. Such installations might also be used to maintain an atmosphere of hydrogen fluoride above the melt, and so to effect a continuous regeneration to compensate for the losses by electrolysis.

The operating temperature range of the cell and the anode material employed are definitely interrelated. The only substances thus far suggested which seem sufficiently inert to fluorine, and also inexpensive enough to be practicable for use as anodes, are nickel and graphite. The former cannot be used at the high-temperature range on account of extreme corrosion, while the latter may not be employed at the lower temperatures, since it is first wet and then physically disintegrated by this kind of bath, which often contains more hydrogen fluoride than the limiting value, already referred to, corresponding to the formula $KF \cdot 1.8HF$. A graphite anode operates smoothly in an anhydrous electrolyte, is scarcely affected by corrosion, cannot contaminate the melt with metal salts, and leads to relatively high current efficiencies, often 80–90 per cent, but it polarizes strongly when the melt contains about 0.3–1.0 per cent water (11, 34) (which may serve as a valuable signal), it may disintegrate physically, and it is somewhat difficult to suspend and to contact efficiently. By comparison, a nickel anode operates smoothly at all times in a medium-temperature bath (thus providing no signal), cannot produce any carbon fluorides, does not disintegrate physically, and is easy to contact and suspend. However, it is seriously corroded under optimum conditions and rapidly otherwise, it contaminates the electrolyte progressively with nickel salts which increase its viscosity, thus promoting explosions and requiring frequent replacements, and it leads to relatively low current efficiencies, often 60–80 per cent under best conditions, and to much lower values (35 per cent or less) otherwise.

In this connection, a recent paper by Ruff (70), summarizing the results of his many years of experience with fluorine chemistry, offers much which is significant and important, although no attempt is made to decide the present question. It is pointed out that when a metal anode is used, a surface layer of fluoride is always formed, thin with nickel, thicker with platinum, but always more or less soluble in the bath, while the fluorine itself is liberated presumably by the thermal decomposition of the fluoride or perfluoride existing at the outside surface. Since the coating is progressively dissolving in the bath, the electrode is gradually consumed. On the other hand, when a graphite anode is employed in a high-temperature cell, the situation is quite different. In this case, if the temperature is much above 250°C., the fluorine penetrates below the surface, expands the crystal lattice of the graphite, and forms the true compound $(CF)_x$ (see above), which has a high resistance. Then the surface temperature rises abruptly, until the $(CF)_x$ decomposes, often with semiexplosive violence, thus exposing a fresh surface, until at last the electrode is disintegrated. According to Ruff, a graphite anode thus penetrated by fluorine is no longer sensitive to polarization by small quantities of water in the melt. However, if a fresh elec-

trode is used and the temperature kept at 250°C. or below, the fluorine does not penetrate into the graphite lattice, but is progressively given off from a thin adsorbed surface layer. Under these conditions the electrode is not disintegrated and is very sensitive to small quantities of water in the melt. Ruff does not believe that the resulting transitory polarization or passivity of the graphite is due to a surface layer of gaseous oxygen, as usually postulated, but rather to the initial formation of $(CF)_x$, catalyzed by the oxygen present. This would seem to be a matter of opinion only, subject to future experimental confirmation.

Taking into consideration all of these factors, the writer now believes that a fluorine generator should have graphite or carbon anodes, and operate on the lower side of the high-temperature range, perhaps from 160–250°C., as recommended by Fredenhagen. Perhaps at some future time carbon rods may become available that do not disintegrate under the conditions required at the medium range, which, under such circumstances, would seem to be more desirable and convenient.

Miscellaneous topics which might be considered at this point are very numerous, so that only a few of the more pertinent ones will be mentioned. The exit tube for the fluorine should always be wide enough and suitably placed to avoid obstruction by solid entrained by the escaping gas. Also, care should be taken in construction to avoid opportunities for the formation of salt bridges across the material insulating the anode suspension. Such formations by-pass part, or even all, of the current, often without producing the appearance of a short circuit, thus reducing the efficiency of the cell and promoting corrosion. As insulating materials for the suspension, a mixture of coarsely ground fluorspar and Portland cement, or a combination of transite and asbestos board washers and rings, seems to be satisfactory, but no material has yet been suggested which is not slowly attacked by the mixture of fluorine and hydrogen fluoride impinging upon it. In addition, it seems appropriate to mention here that in the operation of any fluorine generator, constant care should be taken to make sure that organic vapors cannot diffuse back into or hydrogen accumulate in the anode compartment between runs, especially when the cell is standing at elevated temperatures. Neglect of this precaution can cause sharp anode-chamber explosions when electrolysis is resumed, accompanied by forcible expulsion of the melt and real hazard for the operator. In some rare cases, such explosions may occur as a result of certain other obscure causes difficult to explain, but a certain safety measure in any case is to flush out the anode space with dry air just before throwing the switch.

It is hoped that the foregoing discussion of the factors involved may be of assistance in the development of more practicable and efficient units.

For the convenience of the reader, a fairly complete chronological list of the various generators which have been described in the literature has been compiled in table 2, together with their most important characteristics and the leading references.

If we may now assume, for the purpose of this review at least, that a suitable quantity of fluorine is available at reasonable convenience, the final problem,

TABLE 2

*Fluorine generators which have been described in the literature**

D = diaphragm; U and V refer to the shapes of the units; main construction is of copper unless otherwise indicated

NAME	TYPE	ANODE MATERIAL	TEMPERATURE RANGE	CURRENT EFFICIENCY	REFERENCES	REMARKS
				per cent		
Moissan	U, closed	Platinum–iridium alloy	Low	30	(62) (63)	Original all-platinum unit
Meslans	D	Platinum			(69) (39)	Hollow cooled anode; bottom of container insulated
Gallo	D, closed	Platinum	Low		(38)	Small size, using platinum crucible
Argo, Mathers, Humiston, and Anderson	D, open	Graphite	High	70	(3)	
Ruff	D, closed	Platinum	Low		(72)	Efficiency study interrupted by World War I
Meyer and Sandow	D, open	Graphite	High	68–78	(57)	Graphite container; addition of $NaHF_2$ unsatisfactory
Simons	D, open	Graphite	High		(84) (85)	Inexpensive unit Anode insulated by Portland cement
Lebeau and Damiens	D	Nickel	Medium		(52)	
Bancroft and Jones	D, open	Graphite	High	30	(4)	Magnesium metal container and diaphragm, as suggested by Mathers
Fredenhagen and Krefft	D, closed	Graphite	High	92–94	(34)	
Schumb and Gamble	D, open	Graphite	High		(83)	Similar to that of Bancroft and Jones, but using Monel metal
Dennis, Veeder, and Rochow	V, closed	Graphite	High	45 (5 amp.) 76 (9.3 amp.)	(28, 27)	Insulated cathode

Krekeler	D, closed	Graphite	High	74–77	(50) (12)	Unusual design Magnesium alloy container; electrodes introduced from below and insulated by frozen melt
Bockemüller	D, closed	Graphite	High	70–85	(10)	Insulated cathode
Calcott and Benning	D, closed	Nickel	Low		(97, 95)	Container and insulated cathode of Fe, Ni, Cu, Mg, or other metals or alloys
Denbigh and Whytlaw-Gray	D, open	Graphite	High	About 80	(26)	Large anode insulated by CaF_2 and sodium silicate cement
Miller and Bigelow	U, closed	Graphite	High	80	(60)	Produces 94–99 per cent fluorine by analysis
Aoyama and Kanda	V, closed	Graphite	High	75–90	(2)	Produces 97–99.8 per cent fluorine by analysis
Henne	V, open	Carbon	Medium		(42)	Yields similar to those of Dennis; cathode chamber closed only by notched cork
Cady	D, open	Nickel	Medium	72	(18, 19)	Monel metal unit; later model (19)

* For other reviews on generators, see Lebeau (51), Bockemüller (11), Kienitz and Lange (49), and also an interesting discussion by Cady (19).

to be dealt with in the following section, is to determine quantitatively the composition, and so the purity, of the product.

V. THE QUANTITATIVE ANALYSIS OF ELEMENTARY FLUORINE

It is a strange fact that most of the investigators who have designed and described fluorine generators have told us little or nothing about the quantitative composition of the anode gas produced, yet this may vary over a wide range without giving any readily apparent indication of such change. The phrase "nearly pure," so frequently used, has practically no scientific meaning unless supported by analysis and, as the writer has found to his cost, the fluorine gas issuing from a generator does not speak for itself.

It is believed that the only strictly quantitative method for the analysis of the anode gas from fluorine generators readily available in complete detail, is that described in 1936 by Miller and Bigelow (60), although earlier efforts to analyze this gas by Moissan himself (65), Cuthbertson and Prideaux (23), and Meyer and Sandow (57), as well as later ones by Aoyama and Kanda (2), Cady (18), and Wartenberg (90a), should be noted. Our procedure took advantage of two fundamental facts: namely, that metallic mercury, when agitated, absorbs fluorine quantitatively at room temperature, a fact which has been known since Moissan's time; and that an undisturbed mercury surface exposed to the gas forms a completely protective coating. The apparatus, which consisted essentially of a constant-volume gas buret, is shown to scale, with the surrounding water jacket removed, in figure 3, and the operation will be described by means of a short synopsis of the more important steps in the procedure for the analysis of a sample of fluorine.

The apparatus was first connected at M to a manometer equipped with a levelling bulb, and later at C to the fluorine line by means of a tight, metal, slip joint. At first, mercury was admitted through M and G to F, and the readings on the manometer scale corresponding to the two marks at F and the one at K were observed, with H open. This made it possible to correct later pressure readings at F for a new position of the apparatus relative to the manometer after the former had been demounted and then replaced. After this the capillary above F and the space E were filled with mercury, as indicated in the figure, thus exposing a ring of the metal to the absorption chamber above. Then fluorine was passed in at C and out through A, until the protective coating was formed on the ring above E, and equilibrium completely established. Following this, mercury from B was allowed to flow through D into the exit capillary of the apparatus as shown at A, and the fluorine stream by-passed. After a few minutes the entrance capillary was similarly closed with mercury from B, disconnected at C, and the tips at A and C covered with sealing wax. This gave a sample completely sealed in the absorption chamber in equilibrium at atmospheric pressure and water-jacket temperature. Now the buret was demounted, tipped at an angle, and the mercury repeatedly swirled into contact with the fluorine until the surface of the metal remained bright, which constituted a sharp end point. Finally, the unit was replaced, the final pressure read at F, and the

value corrected by means of the new reading on the manometer scale corresponding to the mark at K, now taken with G closed and H open. From the observed drop in pressure, the percentage of fluorine in the sample could be calculated directly.

In order to analyze the residual gas, if any, mercury was allowed to enter the apparatus through M, G, and E until the pressure inside became approximately atmospheric. Then the unit was connected at B to a gas-analysis apparatus of the Ambler type (1), and the air was cleared from the line by passing mercury in

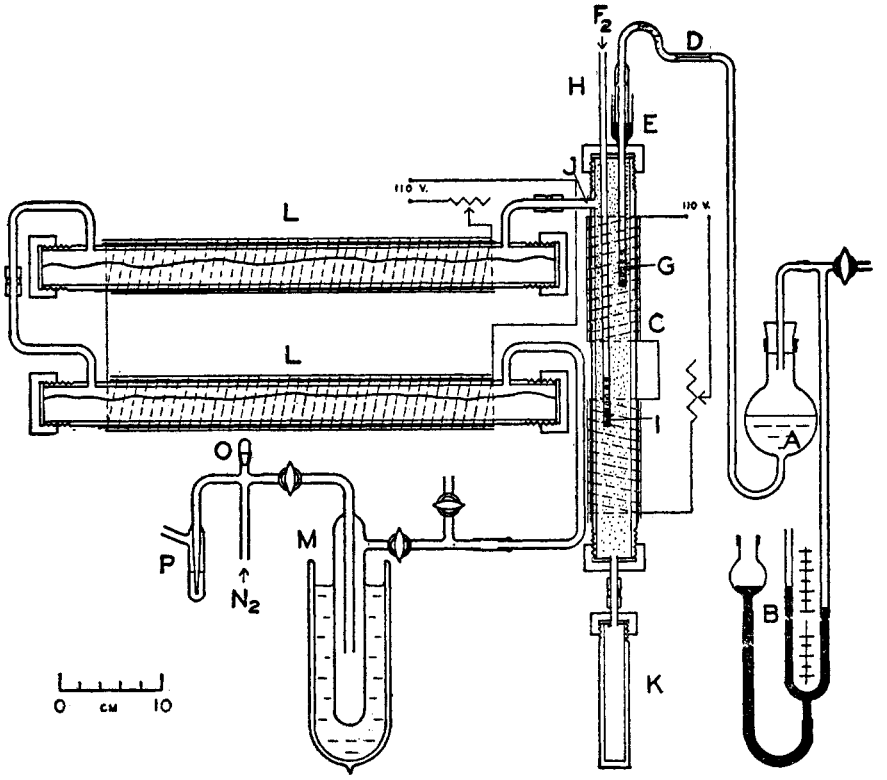


FIG. 3. Constant-volume gas buret for the quantitative estimation of elementary fluorine.

at M, and G, and out from the capillary below C, through D and B. After this the stopcock D was reversed, and the residual gas was led out through the capillary below A, also through D and B into the Ambler apparatus, where it was analyzed for oxygen, carbon dioxide, and inert residue by conventional methods.

As an illustration, a series of analyses of the anode gas from our closed U-type generator (60) is shown in table 3.

The principal error involved in the fluorine analysis was that inherent in making the several manometer readings, and could have a maximum possible

effect upon the final value of approximately ±0.15 per cent, but it was very likely that these errors would be at least partially compensating. Any possible errors due to pressure or temperature equilibrium at the time of sampling, or to changes in the water-jacket temperature during the analysis, or to any volume differential resulting from the formation of mercury fluoride in the buret, have been shown to be entirely negligible. Consequently it seems justifiable to consider that the final values for the volume per cent of fluorine in the sample were accurate to within ±0.1 per cent. This analytical procedure has, however, one definite limitation, which is that the sample must not contain any considerable proportion of oxygen fluoride, which would react slowly with the mercury, making the final value for fluorine only approximate. This condition is always made clearly obvious to the analyst, however, by the fact that in such cases the end point is not sharp, but drifts slowly for a considerable time. Altogether, the analysis just discussed, in the hands of a reasonably trained operator, is

TABLE 3

Composition of the gas produced by the generator vs. the time of electrolysis

NO.	TIME OF ELECTROLYSIS BEFORE SAMPLING		TEMPERATURE OF ELECTROLYTE	PER CENT BY VOLUME OF			
				F_2	CO_2	O_2	Inert
	hr.	*min.*	°C.				
A-1	11	30	265	95.4	1.1	2.2	1.3
B-1	16	30	250	94.8	0.71	3.7	0.79
C-1	25	0	260	94.4	0.63	2.8	2.17
D-1*	7	55	249	97.1	0.97	1.6	0.43
D-2	18	50	256	98.8			
E-1	8	25	251	97.4	1.3	0.98	0.32
F-1	3	30	247	96.5	1.8	1.4	0.30
F-2	23	20	257	99.0	0.22	0.38	0.40

* The procedure for drying the charge with fluorine was introduced just before making run D-1, and the resulting improvement is clearly obvious.

neither difficult nor time-consuming, and may be relied upon to give excellent results.

VI. CONCLUSION

In the foregoing pages an attempt has been made to present (*1*) a detailed description of the various researches dealing with the action of elementary fluorine on organic compounds and free carbon which have appeared in the literature; (*2*) a summary of the theories and mechanisms which have been put forward to explain the observed results; (*3*) a discussion of the construction, operation, and characteristics of five different typical fluorine generators; and (*4*) an outline of a reliable method for the analysis of fluorine gas. In addition, pertinent data regarding compounds and generators have been tabulated for convenient reference. Throughout the presentation, an effort has been made to maintain a critical approach, and to offer some appraisal of the several researches

which have been dealt with. This has been done with a clear understanding of the risks involved in passing a measure of judgment on the work of others, and with due recognition of the writer's own limitations, but it has also been done with the conviction that only in this way could the present review give full value to the thoughtful and discriminating reader.

Fluorine chemistry, including direct fluorination, has been the subject of intensive research, and has undergone great development recently, much of which has not yet been recorded. Enough is known, however, to justify the prediction that all the contributions of the last sixty years to this field, important as they are, may well appear small in comparison with the advances which will be described in the next decade or two. Indeed, should the present work seem to have fulfilled any useful purpose, it is hoped to extend it later on to cover the results of this newest research in the field.

In conclusion, looking toward the future of fluorine in organic chemistry, perhaps a bit of fascinating speculation may not be totally out of place. After all, progress begins in the mind, before it is translated into the laboratory and then the plant. In the past, inorganic chemistry was the chemistry of water solutions, but now we have systems in liquid ammonia, hydrogen sulfide, sulfur dioxide, and many others. Likewise, in the past, organic chemistry has been the chemistry of the hydrocarbons and their derivatives. Now, however, it is becoming more and more possible to envision a new organic chemistry of the fluorocarbons and their corresponding derivatives, including unsaturates, polymers, plastics, refrigerants, insecticides, and even medicinals.

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