# *Fluorine.*

### THE TILDEN LECTURE DELIVERED ON FEBRUARY 19TH, 1942.

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THE first preparation of fluorine will always rank among the triumphs of experimental chemistry. When Henri Moissan commenced his investigations in 1884, the element had long been recognised as a halogen, but all attempts to isolate it by chemical means had failed on account of its high reactivity. The prospect of success must have seemed very slight, but twelve years of painstaking work brought him to his goal, and in 1896 he announced the isolation of fluorine by the electrolysis of a solution of potassium fluoride in anhydrous hydrogen fluoride. The principle of this method, *viz.*, rendering anhydrous hydrofluoric acid conducting by dissolving in it a metallic fluoride, forms the basis of all present-day electrolytic methods, and it is significant that no satisfactory chemical means of preparing fluorine has as yet been found.

The early days of fluorine chemistry proved that the key to success lay in the development of suitable manipulative methods. Moissan was responsible for much progress in this direction, and was able to examine qualitatively many of the reactions of the new element. When, in the period 1902—1904 he gradually turned his attention to other topics, the field was left with its salient features well defined, but with detail still obscure. By a fortunate coincidence an equally gifted experimenter, Otto Ruff, was then at the start of his career, and the new element and its compounds afforded him almost unlimited scope. Ruff made fluorine chemistry his life work, and the school which he created had virtually a monopoly of the subject for some two decades, and indeed has played a leading part right up to the present time.

In selecting Fluorine as the subject for review in this Tilden Lecture, I have had in mind the rapid developments of recent years. Many laboratories now have facilities for experimental work on fluorine and its compounds, and though much remains to be done, there has been for some time a growing interest in both the academic and the technical aspects of the subject. It is my hope that this lecture, which will deal with the all-important experimental aspects of fluorine chemistry, with which I have had some contact, may perhaps interest yet others in this field.

The preparation of fluorine in the laboratory is possible, as far as is known, only by the electrolytic method. Moissan's original cell consisted of a platinum U-tube of about 100 c.c. capacity fitted with fluorite stoppers which carried platinum–iridium electrodes. The electrolyte was a solution of potassium fluoride in anhydrous hydrofluoric acid in the molecular proportion of 1 : 12, and the whole cell was cooled to —30° in order to minimise loss of the low-boiling acid by evaporation (see Moissan, " Le Fluor "). Suitable only for small scale work, this cell was costly to run, for some 6 g. of anode material were dissolved for each g. of fluorine generated. Moissan later substituted copper for platinum as the constructional material of the U-tube and developed cells which gave up to 3 l. of fluorine per hour, but the electrodes were unaltered and the method remained costly and little fitted for general use.

Ruff made only small modifications in the copper cell, and appears to have used it for some 20 years in spite of the need for cooling the electrolyte. Not until 1919 was there any major change, and in that year Argo, Mathers, Humiston, and Anderson published details of a new cell in which the electrolyte was the molten acid potassium fluoride, KF,HF, contained in a copper pot (*J. Physical Chem.*, 1919, **23**, 348). This was a big advance, for, although the principle of Moissan's cell was employed, it was possible to use a carbon anode, which was only slightly attacked at the temperature of operation (240—280°). The copper pot itself was made the cathode and was separated from the anode by a perforated copper diaphragm. Various modified designs for cells using this electrolyte have since been published. We have ourselves obtained highly satisfactory results with a copper cell described by Simons (" Inorganic Syntheses," Vol. I, Editor, H. S. Booth, 1939), which was operated with a current of 10 amps. at about 8 volts. It was possible by increasing the cell dimensions and by employing a group of three graphite rods for the anode to run it at 30 amps. A further point of interest is that an insulating cement for the anode made by drying a paste of calcium fluoride and sodium silicate (Denbigh and Whytlaw-Gray, *J. Soc. Chem. Ind.*, 1934, **53**, 139) has proved itself superior to Portland cement, which was recommended by Simons.

There is little to indicate the relative merits of other cells charged with $KHF_2$ which have been described. A V-shaped cell constructed of copper tubing described by Dennis, Veeder, and Rochow (*J. Amer. Chem. Soc.*, 1931, **53**, 3263) should prove useful for the small-scale production of fluorine. Schumb and Gamble (*ibid.*, 1930, **52**, 4302) have used a cell constructed of Monel metal, but otherwise similar to the Simons cell. These authors' statement that copper does not resist attack by the molten electrolyte is not, however, borne out by our experience. The nickel cell described by Miller and Bigelow (*ibid.*, 1936, **58**, 1585) has the advantage that it is closed by a tightly fitting lid which protects the electrolyte from atmospheric moisture. This is a matter of great importance when pure fluorine is required, for a damp electrolyte gives gas contaminated with oxygen, ozone, and fluorine monoxide in addition to carbon and silicon fluorides. Other cells operating in the same temperature range are constructed of silver (Fredenhagen, *Z. Elektrochem.*, 1929, **35**, 670), magnesium (Jones, *J. Physical Chem.*, 1929, **33**, 801), or graphite (Meyer and Sandow, *Ber.*, 1921, **54**, 759; Fichter and Humpert, *Helv. Chim. Acta*, 1926, **9**, 467), but it is not apparent that they have any special advantages.

As an alternative to the acid fluoride $KHF_2$, a second acid fluoride KF,3HF (m. p. 65°) may be used. This was first suggested by Lebeau and Damiens (*Comp. rend.*, 1925, **181**, 917). It is prepared in the fluorine cell as required by the addition of the requisite quantity of anhydrous hydrogen fluoride to potassium fluoride or its monoacid salt. This can be done only if the anhydrous acid is readily available in quantity, but, if so, the preparation and regeneration of the electrolyte are comparatively simple matters. A convenient cell operating in this way is described by Cady (" Inorganic Syntheses," Vol. I, p. 142), and has an outer Monel-metal pot, which is made the cathode, a copper diaphragm, and a nickel anode. The use of a metal electrode eliminates a major drawback of the high-temperature cell, *viz.*, the formation of carbon fluorides in the course of the electrolysis. Mild steel can replace Monel for the outer vessel, as it has a high resistance to attack by either the electrolyte or gaseous fluorine. This type of cell is best constructed with a closed lid and should be fitted on both the anode and the cathode side with a coil cooled in solid carbon dioxide to condense and return hydrogen fluoride vapour to the electrolyte. Several modifications have been described, but the only one calling for special mention is that of Henne (*J. Amer. Chem. Soc.*, 1938, **60**, 96), who has developed a particularly robust V-shaped unit made of copper tubing, with graphite electrodes. Simplification of the cell so as to allow a rapid interchange of anode made it possible to overcome the difficulty arising from the formation of a glassy silicate coating on the anode. This arises from silicates contained in acid potassium fluoride, and its removal by a preliminary electrolysis, followed by the insertion of a fresh graphite anode, greatly simplifies the production of fluorine from the salt KF,3HF.

Progress in the laboratory leads naturally to the enquiry as to whether fluorine can be made on a large scale and, what is more important, whether there is any major industrial use for it. The patent literature is usually an unsatisfactory guide to industrial practice, but it is quite evident that cells operating with the two types of electrolyte mentioned above have been closely considered, if indeed such cells have not been used. Important details such as the insulation of the electrodes and the construction of low-resistance diaphragms for cells taking a high current have been covered by patents, and the difficulties in making fluorine on a large scale should be no greater than those encountered with other fused electrolytes, particularly as the use of mild steel as a constructional material is possible. Whether or not fluorine is made in quantity depends much more on its potential applications. At present these are non-existent, but it is possible that further progress may lead ultimately to the establishment of a major industry.

Before reviewing the reactions of gaseous fluorine, we may consider briefly the laboratory manipulation of the element. It attacks soft glass rapidly, and although Pyrex has a certain resistance it is slowly corroded, especially at points where it has been worked in the blowpipe. For most purposes therefore the use of glass apparatus is inadvisable and one has to employ either metals or fused silica. There is as yet comparatively little information about the resistance of plastics to fluorine. Copper and steel tubing joined by screwed, sleeve, or flanged joints are completely satisfactory for operations with the dry gas, and tubes of the same materials may also be used in studying many reactions. Fused silica is equally resistant to gaseous fluorine, and apparatus constructed entirely of this material is best used when it is desired to purify the gas by liquefaction and fractionation. This type of manipulation is well illustrated by Kanda's work on the properties of liquid fluorine at low temperatures, in which a number of the physical properties, including the vapour pressure, viscosity, and surface tension, were studied (*Bull. Chem. Soc. Japan*, 1937, **12**, 409, 416, 455).

Up to 200—300° the common metals resist attack by fluorine, but at higher temperatures the platinum metals must be employed. Above a red heat, free fluorine is so reactive that only vessels specially constructed of moulded fluorite will resist it (cf. Ruff and Riebeth, *Z. anorg. Chem.*, 1928, **173**, 373; 1929, **179**, 166). Fortunately, the high reactivity of fluorine is not shared by the majority of its compounds, which for the most part may be handled in glass apparatus. Some, however, are as reactive as, or more reactive than, fluorine itself and necessitate the use of fused silica or metal apparatus. A number of the substances discussed fall within this class, and further reference will be made to their manipulation.

Among the reactions of fluorine with the non-metals, the direct formation of fluorides of the other halogens is of particular interest because of their great reactivity. The discovery of the chlorine fluorides was in a sense accidental. In the course of experiments on the fluorination of uranium and the platinum metals by fluorine–chlorine mixtures, Ruff found that explosions in the gas mixture sometimes occurred. They were traced to an exothermic reaction between the two halogens, which were found to react explosively when sparked : indeed, it was even possible to burn fluorine in chlorine. Two reaction products, ClF and $ClF_3$, which were similar in type to known interhalogen compounds were subsequently isolated, and fluorides both of bromine and of iodine were also obtained, the boiling points of which are shown in Table I.

TABLE I.

*Boiling Points of the Halogen Fluorides.*

|  | B. p. |  | B. p. |  | B. p. |
|---|---|---|---|---|---|
| ClF | −100·1° | BrF | *ca.* 20° | — | — |
| $ClF_3$ | 12·1 | $BrF_3$ | 127 | — | — |
| — | — | $BrF_5$ | 40·5 | $IF_5$ | 97° |
| — | — | — | — | $IF_7$ | 5·5 |

The chlorine fluorides are readily prepared by passing a mixture of the two halogens through a copper reaction vessel heated to 250° (Ruff *et al.*, *Z. anorg. Chem.*, 1928, **176**, 258; 1930, **190**, 270; 1932, **207**, 46; *Z. angew. Chem.*, 1928, **41**, 1289. See also Fredenhagen and Krefft, *Z. physikal. Chem.*, 1929, **141**, 221). An equilibrium mixture results in which the ratio ClF : $ClF_3$ is about 4 : 1. The difference in boiling points is so great that separation by fractional distillation and condensation in a series of fused silica condensation traps is a simple matter. Copper and steel vessels are also quite serviceable, although glass is rapidly attacked. The bromine fluorides are prepared and purified in much the same way by mixing in a copper tube streams of fluorine and of bromine vapour carried by nitrogen (Ruff *et al.*, *Z. anorg. Chem.*, 1931, **202**, 49; 1932, **206**, 59; 1933, **214**, 81, 91). The tube becomes warm at the point where the gases mix, and under these conditions the trifluoride is the chief product. At 250° the pentafluoride is formed, and at 0° the unstable monofluoride results. Of the iodine derivatives, the pentafluoride was first prepared by Gore by the reaction of iodine and silver fluoride (*Phil. Mag.*, 1871, **41**, 308). It is, however, more readily prepared in a pure state by the direct fluorination of iodine, and it was while preparing the compound by this means that Ruff and Keim noticed the formation of small amounts of an iodine–fluorine compound which was more volatile than the pentafluoride. When this observation was followed up, the preparation of a heptafluoride by heating the vapour of the pentafluoride with fluorine to 250° in a platinum apparatus was soon accomplished (*Z. anorg. Chem.*, 1930, **193**, 176).

These compounds are remarkable, for their reactivity exceeds that of fluorine itself. As Ruff showed, they react explosively with most organic substances, and numerous inorganic compounds either inflame or react with great vigour. This may be demonstrated by pouring bromine trifluoride on wood, which immediately inflames at the point of contact, or on asbestos, which becomes incandescent. The primary reaction is in each case fluorination and not oxidation.

Fluorides of other non-metallic elements also have many interesting properties, as regards both their constitution and their stability. With the exceptions of nitrogen and the rare gases, all non-metals react directly with fluorine, though there may be alternative methods of preparing their fluorides (see below). In Table II the formulæ of the chief non-metallic fluorides are given, together with their boiling points in parentheses. They are in general very much more volatile than the corresponding chlorides. In the higher fluorides, too, the maximum valency of the element is invoked.

TABLE II.

*Fluorides of the Non-metallic Elements.*

| Element. | Fluorides. |
|---|---|
| B | $BF_3$ (−101°) |
| C | $CF_4$ (−130°), $C_2F_6$ (−78°), $C_3F_8$, etc., $C_2F_4$ (−76°) |
| Si | $SiF_4$ (sublimes −95·7°) |
| N | $NF_3$ (−130°) |
| P | $PF_5$ (−84·5°), $PF_3$ (−101°) |
| As | $AsF_5$ (−53°), $AsF_3$ (60·4°) |
| O | $OF_2$ (−144·8°), $O_2F_2$ (—), $O_3F_2$ (—) |
| S | $SF_6$ (sublimes −63·8°), $SF_4$ (−40°), $S_2F_2$ (?), $SF_2$ (?) |
| Se | $SeF_6$ (sublimes −46·6°), $SeF_4$ (90·5°) |
| Te | $TeF_6$ (sublimes −38·9°) |

Of these fluorides, the first, boron trifluoride, calls for little comment. It is formed by fluorinating boron : the reaction has not been closely studied and it is possible that by working up large quantities of the product other less volatile boron fluorides might be isolated. The laboratory preparation of the trifluoride is more simply carried out by the action of concentrated sulphuric acid on a mixture of sodium fluoborate and boric oxide. The compound is used technically as a catalyst in organic condensation reactions.

Carbon fluorides are best obtained by direct fluorination of the element, though they also result from the high-temperature fluorination of many organic compounds. Carbon will burn if it is strongly heated in fluorine, and this reaction was shown by Moissan to yield mainly the tetrafluoride. It has been more completely studied by Ruff and his co-workers (Ruff and Keim, *Z. anorg. Chem.*, 1930, **192**, 249; Ruff and Bretschneider, *ibid.*, 1934, **217**, 1), who observed that when carbon was heated in a stream of fluorine under conditions such that it did not ignite, violent explosions were liable to occur. These were traced to the explosive decomposition of a solid carbon monofluoride $(CF)_n$, which results when graphite is saturated with fluorine at 420°. Particular interest attaches to the structure of this solid fluoride, for *X*-ray examination has shown it to be an interstitial compound formed by the introduction of fluorine atoms between the basic planes of the graphite lattice. The spacing of the latter is increased by the presence of fluorine from 3·40 to 8·17 A., and this naturally leads to a considerable swelling of the solid. Carbon monofluoride may also be formed from the graphite anode of a fluorine cell, if the latter is operated at too high a temperature and under polarising conditions, and is probably an intermediate in the formation of carbon fluorides when the cell is operating normally.

In the decomposition of carbon monofluoride or the direct fluorination of carbon, Ruff showed that a mixture of fully fluorinated hydrocarbons was formed. These ranged in composition from $CF_4$ to $C_6F_{14}$ and included $C_2F_4$, though no aromatic derivatives were obtained. The full study of these interesting substances is, however, due to Simons and Block (*J. Amer. Chem. Soc.*, 1939, **61**, 2962), who discovered that the direct fluorination of solid carbon may be conducted without risk of explosion if the carbon is first impregnated with 1% of a mercury salt. No explanation of the action of the latter has been offered. The products, which were collected in quantity and carefully separated, ranged in composition from $CF_4$ to $C_7F_{16}$ and all shared the remarkable chemical inertness of carbon tetrafluoride. The name fluorocarbons has been given to the series, which clearly bears more than a superficial resemblance to the aliphatic hydrocarbons. Unsaturated fluorinated hydrocarbons and carbon chlorofluorides, it may be noted, do not share the inertness of the fluorocarbons. There is also no indication that an analogous series of silicon fluorides exists, for attempts to prepare octafluorosilicopropane have invariably resulted in the breaking of the Si–Si linkage (unpublished experiments by C. J. Wilkins).

Of the fluorides of Group VB elements, nitrogen trifluoride is especially interesting because of its low reactivity. It was among the first fluorine compounds which Ruff attempted to isolate in 1903 (Ruff and Geisel, *Ber.*, 1903, **36**, 2677; Ruff, Fischer, and Luft, *Z. anorg. Chem.*, 1928, **172**, 417), but it was not until 25 years later that he obtained it by electrolysis of the molten acid ammonium fluoride $NH_4F,HF$ in a copper cell with a graphite anode. Two other compounds, $NH_2F$ and $NHF_2$, which are formed in small amounts in the course of the electrolysis, are both reactive and toxic, and are much closer to nitrogen trichloride in their properties. The stability of the trifluoride is associated with a positive heat of formation which in turn depends on the N–F bond characteristics.

It is hardly necessary to dwell at great length on the properties of the fluorides of the remaining non-metallic elements. The oxygen fluorides are comparatively new to chemical literature and it is interesting to recall that the simplest of them, $F_2O$, is formed in appreciable quantities whenever a fluorine cell is operated with a moist electrolyte. Not until 1927 was this fact realised (Lebeau and Damiens, *Compt. rend.*, **185**, 652), however, and then the new oxide was quickly prepared and characterised (*idem, ibid.*, 1929, **188**, 1253; Ruff and Menzel, *Z. anorg. Chem.*, 1930, **190**, 257; 1931, **198**, 39; Dennis and Rochow, *J. Amer. Chem. Soc.*, 1933, **55**, 2931; Cady, *ibid.*, 1935, **57**, 246). Its formation by bubbling a stream of fluorine through a 2% solution of sodium hydroxide by means of a platinum tube dipping just below the surface of the liquid is remarkably simple once a fluorine cell is in operation, and since the gas does not attack glass it may readily be manipulated by the usual vacuum methods. The inertness of fluorine monoxide when compared with chlorine monoxide is also striking, for the former does not under any conditions explode though it is a strong oxidising agent. The other fluorine oxides are less stable, though they too are non-explosive. The oxide $F_2O_2$ is formed when a mixture of fluorine and oxygen is passed through an electrical discharge in a silica tube cooled in liquid air (Ruff and Menzel, *Z. anorg. Chem.*, 1933, **211**, 204) and is stable only below $-40°$. Above this temperature it decomposes into a mixture of fluorine and oxygen. The same is true of the oxide $F_2O_3$, which is said to be formed when a mixture of liquid fluorine and liquid oxygen is exposed to ultra-violet light (Aoyama and Sakuraba, *J. Chem. Soc. Japan*, 1938, **59**, 1721). None of the oxyacids of fluorine or their salts have so far been satisfactorily characterised, though some indications of their existence have been obtained (Dennis and Rochow, *J. Amer. Chem. Soc.*, 1932, **54**, 832; Cady, *ibid.*, 1934, **56**, 1647; Ruff, *Ber.*, 1936, **69**, 181). This is a point which needs closer investigation, for it is hardly conceivable that oxyacids are not formed under suitable conditions.

Sulphur, selenium, and tellurium all yield several fluorides, the best known being the hexafluorides $SF_6$, $SeF_6$, and $TeF_6$. These share with the little-known compound $S_2F_{10}$, described by Denbigh and Whytlaw-Gray (J., 1934, 1346), a high measure of chemical inertness which is similar to that of nitrogen trifluoride. All are formed by direct fluorination of the respective elements, though disulphur decafluoride results only in very small yields. The lower fluorides are far more reactive, though their chemical investigation is as yet far from complete.

With regard to the metallic fluorides, it will be evident that for the most part they may be produced without the aid of elementary fluorine; indeed, many were known long before fluorine was isolated and are much more readily formed by the use of hydrofluoric acid. One feature of the reaction of fluorine with the metals may, however, be mentioned, as it illustrates an important characteristic of the element. The metals react to give fluorides in which the maximum covalency is operative. Examples are compounds such as argentic fluoride, cobaltic fluoride, and the higher fluorides of the platinum metals. Neither bivalent silver nor tervalent cobalt salts are normally formed unless the higher valency state is stabilised by co-ordination. On the other hand, passage of fluorine over either silver or cobaltous chloride results in an exothermic reaction and complete conversion of the chloride into the higher fluoride of the metal. These two compounds are among the most readily available of the higher fluorides and they may be used as fluorinating agents.

The fluorides of the platinum metals, the formulæ of which are given in Table III (Ruff, *Ber.*, 1936, **69**, 188), illustrate still further the tendency to form high-valency metallic fluorides, which is so strong, indeed,

TABLE III.

*Fluorides of the Platinum Metals.*

| | | | | | |
|---|---|---|---|---|---|
| $RuF_5$ | $RhF_{4-5}$ | | $OsF_8$ | | |
| | $RhF_3$ | $PdF_3$ | $OsF_6$ | $IrF_6$ | |
| | | $PdF_2$ | $OsF_4$ | $IrF_4$ | $PtF_4$ |
| | | | | | $PtF_2$ |

that difficulty is experienced as a rule in obtaining lower fluorides. Some of the fluorides are very volatile, iridium hexafluoride, for example, boiling at 53°. The constitution is governed primarily by the possibility of packing the relatively small fluorine atoms round the metal atom. The higher fluorides evolve fluorine when strongly heated, though the temperature of decomposition is usually so high that the containing vessel is attacked.

Direct fluorination of organic compounds was thought until comparatively recently to result always in vigorous or explosive reactions, accompanied by charring, and accordingly was not considered as a means of preparing organic fluorides. Recent investigations have shown, however, that the reactions can be moderated and indeed made to give useful yields of certain products. The first experiments of this sort were made by Humiston (*J. Physical Chem.*, 1919, **23**, 572), who sought to control the reaction of fluorine with various inorganic substances by dilution with nitrogen or carbon dioxide. The past ten years have seen a renewed and far more successful attack on the problem, particularly by Bigelow and his co-workers (*J. Amer. Chem. Soc.*, 1933, **55**, 4614; 1934, **56**, 2773; 1937, **59**, 198, 2072; 1938, **60**, 427; 1939, **61**, 3552; 1940, **62**, 267, 1171, 3302; 1941, **63**, 788). Their first experiments involved fluorination of aromatic compounds suspended or dissolved in carbon tetrachloride in a massive copper apparatus. This gave complex mixtures of products and the solvent was slowly attacked. In later experiments a method of vapour-phase fluorination was evolved, a stream of fluorine diluted with nitrogen being allowed to react with a gaseous organic compound, or an organic vapour, in a metal tube packed with copper gauze. This procedure eliminates all risk of explosions, which otherwise occur, and has given products which, though usually complex, have as a rule been fully characterised. Among the substances so far fluorinated are methane, ethane, ethyl chloride, acetone, and hexachlorobenzene. From ethyl chloride, to quote one example only, the products were $CF_4$, $CF_3Cl$, $CF_3{\cdot}CF_2Cl$, $CF_2{:}CCl_2$ and $CHF_2{\cdot}CH_2Cl$. Some at least of these substances are useful as refrigerants (see below), and it is evident that the method may, when further developed, acquire technical importance.

Bigelow's work has resulted in one of the few attempts to account for the mechanism of a reaction in which fluorine takes part; the fluorination of acetone, which gives a complex mixture of products, is satisfactorily represented by the following mechanism :

$$\begin{aligned} &F_2 &&= 2F \text{ (catalytic or thermal)}\\ &CH_3{\cdot}CO{\cdot}CH_3 + F &&= CH_3{\cdot}CO{\cdot}CH_2 + HF\\ &CH_3{\cdot}CO{\cdot}CH_2 + F_2 &&= CH_3{\cdot}CO{\cdot}CH_2F + F \end{aligned}$$

This cycle is repeated until the fully fluorinated compound $CF_3{\cdot}CO{\cdot}CF_3$ is produced, after which the reactions (1)—(5) are postulated, and will account for the other observed reaction products :

$$\begin{aligned} &(1)\ CF_3{\cdot}CO{\cdot}CF_3 + F = CF_3{\cdot}CO + CF_4 \qquad &&(4)\ COF + F_2 = COF_2 + F\\ &(2)\ CF_3{\cdot}CO + F_2 = CF_3{\cdot}COF + F &&(5)\ 2COF = (COF)_2\\ &(3)\ CF_3{\cdot}COF + F = CF_4 + COF && \end{aligned}$$

It would be misleading to refer to the use of elementary fluorine for the preparation of either organic or inorganic fluorides without at the same time outlining some at least of the alternative methods of fluorination. These are as important as, and, in general, a great deal more convenient than, the use of elementary fluorine, and include the reaction of halogenated compounds with metallic fluorides and also the use of hydrogen fluoride.

The outstanding fluorinating reagent is antimony trifluoride, which was first used by the Belgian chemist Swarts for replacing chlorine or bromine by fluorine in organic molecules. It is now known to afford an equally convenient way of preparing fluorides of other non-metals, though it is by no means general in its action. For instance, when phosphorus trichloride is refluxed with excess of antimony trifluoride together with a little antimony pentachloride, which acts as a catalyst, a good yield of phosphorus trifluoride is obtained. If, on the other hand, ethyldichloroamine is similarly treated, no fluorination results. Such differences in the ease of fluorination are also very marked in organic compounds, and the causes which determine whether a particular chlorine atom can be replaced by fluorine or not are still obscure.

An interesting property of antimony trifluoride, not shown by other metallic fluorides, is its capacity for producing step-wise fluorination of chlorinated or brominated derivatives of the non-metals. A deficit of the fluoride is used, and the reaction between it and a liquid halide is conducted at a suitably reduced pressure, whereupon the partly fluorinated products, which are more volatile than the parent halide, escape as they are formed. They may be further separated by distillation through a low-temperature fractionating column, or by fractional condensation and distillation in a vacuum. As may be seen from the data given below for typical mixed halides, a number of which have been prepared by Booth and his co-workers, the physical properties are intermediate between those of the parent halide and the fluoride. The chemical properties of these compounds are not in every case known, but in some at least the fluorine is less reactive than the other halogen. (For bibliography, see *Ann. Reports*, 1940, **37**, 150.)

Modifications of technique make it possible to use the Swarts reaction for fluorinating gases and vapours; *e.g.*, silyl chloride, $SiH_3Cl$, and silylene chloride, $SiH_2Cl_2$, have been fluorinated by attaching a large bulb containing antimony trifluoride and pentachloride to the vacuum apparatus used in preparing the chlorosilanes, and distilling into the bulb measured quantities of the latter (Maddock, Emeléus, and Reid, *Nature*, 1939, **57**, 1333). Reaction occurs at room temperature and the respective products, $SiH_3F$ (b. p. −98·6°)

and $SiH_2F_2$ (b. p. −77·8°), are subsequently purified and characterised in the vacuum apparatus. A similar technique could probably be used for the preparation of a variety of volatile fluorine derivatives of this class, since such compounds do not as a rule attack glass.

TABLE IV.

*Typical Fluorinated Derivatives of Non-metallic Halides.*

| Parent halide. | Derivative. | M. p. | B. p. | Parent halide. | Derivative. | M. p. | B. p. |
|---|---|---|---|---|---|---|---|
| $SiCl_4$ | $SiF_4$ | −90° (1318 mm.) sublimes | −95·7° | $PBr_3$ | $PF_2Br$ | −135·8° | −16·1° |
|  | $SiF_3Cl$ | −142·0 | −70·0 |  | $PFBr_2$ | −115·0 | 74·8 |
|  | $SiF_2Cl_2$ | −139·7 | −32·2 | $POCl_3$ | $POF_3$ | −39·4 | −39·8 |
|  | $SiFCl_3$ | −120·8 | 12·2 |  | $POF_2Cl$ | −96·4 | 3·1 |
| $PCl_3$ | $PF_3$ | −151·5 | −101·1 |  | $POFCl_2$ | −80·1 | 52·9 |
|  | $PF_2Cl$ | −164·8 | −47·3 | $PSCl_3$ | $PSF_3$ | −148·8 | −52·3 |
|  | $PFCl_2$ | −144·0 | 13·85 |  | $PSF_2Cl$ | −155·2 | 6·3 |
|  |  |  |  |  | $PSFCl_2$ | −96·0 | 64·7 |

Antimony trifluoride is also used in preparing technically-useful organic compounds, the most important of which are the mixed halogen derivatives of the simple aliphatic hydrocarbons. The fluorochloromethanes and related compounds, which are known collectively as " Freons," are used as refrigerants. They possess a convenient range of boiling points (Table V), have suitable thermal properties, and are in addition non-toxic and non-corrosive. The greatly increased use of refrigerating and air-conditioning plant created a demand for new materials and this was met by the properties of the Freons (Midgley and Henne, *Ind. Eng. Chem.*, 1930, **22**, 542). It is interesting to recall that some of these compounds were prepared many years earlier by Swarts. It seems to have been generally assumed that they were reactive and toxic; once these ill-founded ideas had been dispelled, the technical possibilities of the Freons were vigorously explored. The literature of the last twelve years contains many references to the production of new members of the group by the action either of antimony trifluoride or of this substance and anhydrous hydrogen fluoride on chloro- or bromo-derivatives of hydrocarbons.

TABLE V.

*Boiling Points of Typical " Freons."*

| Compound | $CHClF_2$. | $CCl_2F_2$. | $CHCl_2F$. | $CCl_3F$. | $CCl_2F{\cdot}CCl_2F$. |
|---|---|---|---|---|---|
| B. p. | −40·8° | −29·8° | 8·9° | 23·7° | 47·6° |

A second application of the Swarts reaction arises from the discovery that the $CF_3$ group in a dye has a strong hypsochromic action, *i.e.*, instead of deepening the shade of the dye, as do most substituents, it brightens it. This would be of little value were it not that this group is particularly stable : indeed, its stability approaches that of carbon tetrafluoride itself. Benzotrichloride is typical of the starting materials used : it is converted into benzotrifluoride either by antimony trifluoride or by anhydrous hydrofluoric acid, and the fluorinated compound is then nitrated, reduced, diazotised, and coupled. This constitutes only a minor use of fluorine compounds, and, since few fluorinated substituents are likely to exhibit the stability of the $CF_3$ group, extensive developments are hardly to be expected.

Many fluorinating agents other than antimony trifluoride have been used in preparing both inorganic and organic fluorides. Anhydrous hydrogen fluoride, and the fluorides of silver, potassium, mercury, zinc, thallium, lead, and ammonium are among the chief, and of these, hydrogen fluoride is certainly the most important. The commercial production of the anhydrous acid is a comparatively recent development; indeed, before 1930 it was usually prepared in the laboratory by heating potassium hydrogen fluoride. The present method is based on the controlled reaction between calcium fluoride and sulphuric acid, followed by fractional distillation of the hydrogen fluoride evolved, and the anhydrous acid is stored in steel tanks and cylinders, and can be manipulated with steel pipes and valves.

Applications so far suggested are mostly in the preparation of organic compounds, for hydrogen fluoride has proved to have extremely useful properties as a catalyst for alkylation, acylation, and polymerisation reactions (cf. Simons, *ibid.*, 1940, **32**, 178). In this field it is able to promote a wide range of reactions which are normally brought about with the aid of metal halides, sulphuric acid, or phosphoric acid as condensing agents. In such cases the products contain no fluorine. Hydrogen fluoride is, however, also used in preparing organic fluorides; *e.g.*, in addition to the reactions already mentioned in connection with the preparation of Freons and dyes, it will convert acid chlorides into acid fluorides and may be induced to add on to double bonds. Were the products of any particular value, there is little doubt that the uses of the acid would undergo very rapid development.

There has been up till now no systematic study of the fluorinating action of metallic fluorides other than antimony trifluoride. Argentic fluoride and cobaltic fluoride are among the strongest, and normally cause charring when refluxed with organic compounds. Mercuric fluoride is milder in its action, and the chlorofluoride and mercurous fluoride even more so. The fluorides of potassium, silver, zinc, thallium, lead, and ammonium are all mild and will normally give complete fluorination when refluxed with substances such as non-polar halides or organic acid chlorides, but not with aliphatic chloro-compounds. There are, however, many gaps in our present knowledge of the action of these compounds, and one frequently finds that only one fluorinating agent has been examined for a particular reaction.

The technique of fluorination with inorganic fluorides is very simple. Sometimes a reaction between a gas and the solid fluoride is brought about, as, for example, when cyanogen iodide vapour is distilled over heated silver fluoride in the preparation of cyanogen fluoride, or when nitrosyl chloride is converted into nitrosyl fluoride by the action of silver fluoride. Nitrosyl fluoride is extremely reactive, and here the reaction must be carried out in fused silica apparatus, but cyanogen fluoride may be prepared in glass. The preparation of the new aryl and alkyl fluorides of silicon, selenium, and tellurium (unpublished experiments by C. J. Wilkins and A. G. Heal, Imperial College), which are shown in Table VI, illustrates still further the potentialities of these metallic fluorides as fluorinating agents.

TABLE VI.

*Aryl and Alkyl Fluorides of Silicon, Selenium, and Tellurium.*

| | | | |
|---|---|---|---|
| $SiPh_3F$ | $SiEt_2F_2$ | $SePh_3F$ | $TePh_3F$ |
| $SiPh_2F_2$ | $SiEtF_3$ | $SePh_3F,HF$ | $TePh_2F_2$ |
| $SiPhF_3$ | | $SePh_3F,2HF$ | $TeMe_3F$ |
| | | | $TeMe_2F_2$ |

All of the silicon derivatives were prepared in good yield by heating the corresponding aryl- or alkyl-silicon chloride with zinc or antimony fluoride, a reaction which is comparable with the preparation of the normal fluorides or chlorofluorides. No indication of the formation of chlorofluorides was obtained, however, though this may be due to inadequate control of the reaction conditions. Triphenylselenium fluoride was prepared by treating the chloride in aqueous solution with silver fluoride, and the addition products, which were well crystallised, were formed by further treatment of the monofluoride with hydrofluoric acid. The tellurium compounds were obtained by the non-ionic reaction of silver fluoride with the corresponding iodo-compounds in toluene or acetone ($TePh_2F_2$ and $TeMe_2F_2$), or by the action of aqueous hydrofluoric acid on $TePh_3OH$ and $TeMe_3OH$ ($TePh_3F$ and $TeMe_3F$).

The unsolved problems in fluorine chemistry are many. Great as has been the progress made in the last twenty years, there are still numerous fluorides which have so far resisted attempts at preparation, and there is scope for improvements in the technique of handling highly reactive fluorine compounds. Up till now, physicochemical problems relating to the reactions of fluorine have not even been considered, and important data for the bond distances and energies in many fluorides are still lacking. Lastly, we cannot but suppose that in the vast range of organic fluorine compounds which have been made, or may be made, there will prove to be some at least which will have valuable properties and will provide adequate justification for the full development of this field.