

Chapter 3

INORGANIC FLUORINE CHEMISTRY, 1900-1945

O. GLEMSER

Universität Göttingen, Institut für anorganische Chemie, Tammanstrasse 4, D-3400, Göttingen (F.R.G.)

General

Introduction

The rapid development of inorganic fluorine chemistry began after elementary fluorine had been produced for the first time by Moissan; the entire field of inorganic chemistry was given such a strong impetus by his work that the remarkable revival which followed overcame the stagnation besetting developments at around the turn of the century.

Although many fluorine compounds had been produced before Moissan, it was often difficult to identify and characterise them. This state of affairs now changed. New methods were required suitable for handling elementary fluorine and the new fluorides which were attained with its help, and which often showed unusual chemical properties. Special procedures and equipment had to be devised for the production of compounds, their purification and analysis, and also for the study of their physical and chemical properties. Furthermore, it became clear that in many cases the materials employed for the instruments and equipment then commonly used did not satisfy the needs of fluorine chemistry; the initial complications were, however, overcome in the course of time.

The same problems existed in solid-state fluorine chemistry at this time as in solid-state chemistry in general. It was not until the 1920s that solid phases could be distinguished and structures determined with the help of X-ray structure analysis. In the 1930s it became possible to determine the structures of gaseous fluorides by electron diffraction. These years also witnessed the application of vibrational spectroscopic methods.

Moissan had already had some success in developing equipment and materials during his research on the new element.* He examined qualitatively a great many reactions of fluorine. After he had turned to other areas of research, the gifted experimentalist Otto Ruff began the work which was to

*Moissan reported [1, 2] that the colour of fluorine gas was a clear greenish-yellow. Some doubts have been expressed since, suggesting that this colour may have been due to impurities. However, a very recent re-examination [3] has confirmed Moissan's observation. The colour of a long column of gaseous fluorine was found to be yellow, and not particularly greenish, in both daylight and artificial light. The colours recorded in Moissan's original Paper [1] and in the recent report [3] are reproduced below (Figs. 3.1, 3.2).

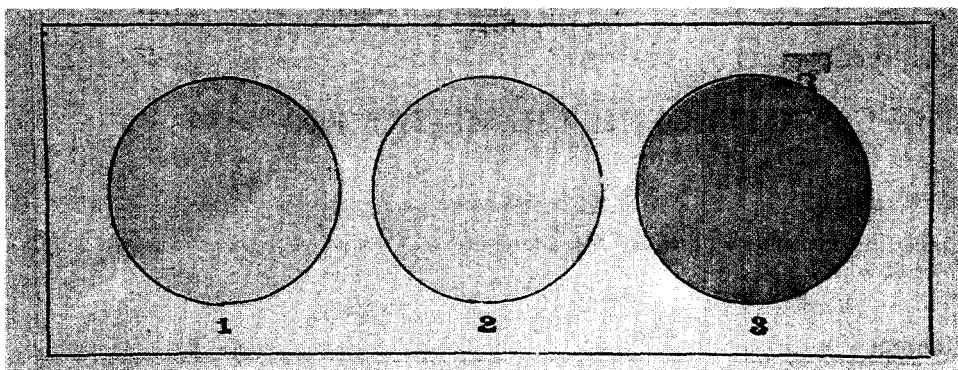


Fig. 3.1. Moissan's original colour discs; 1, air-filled 1 m tube; 2, tube filled with fluorine; 3, tube filled with chlorine.

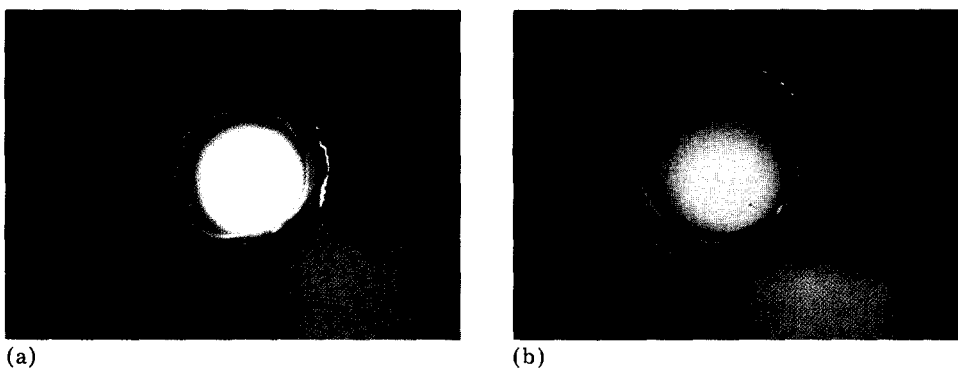


Fig. 3.2. Evidence of molecular fluorine in a 5 m tube. (a), air-filled tube; (b) same tube filled with fluorine at atmospheric pressure.

make him one of the leading fluorine chemists of his time. Ruff [who was professor of inorganic chemistry at the Technische Hochschulen of Danzig (1904 - 16) and Breslau (1916 - 39)] had a lasting influence on preparative techniques employed in the chemistry of fluorine. He developed equipment for the production and the characterisation of new and already known compounds, such as that for melting points and boiling points (Ruff and Clusius; 1930*), vapour pressures (Ruff and Le Boucher; 1934) and heats of formation (Ruff and Wallaner; 1931). He also developed seals, fluorine-resistant boats and tubes as well as condensation vessels and much more. Many of the melting and boiling points which he determined can be found unchanged in the contemporary literature.

What made Ruff interested in the chemistry of fluorine? As a young inorganic chemist he was interested in geological problems. He hoped to determine the titanium content of silicates, *i.e.* the estimation of Ti and Si in

*The exact publication dates of the authors' work referred to in the text may be found in the various reviews listed in the References at the end of this chapter.

each other's presence. He thought that the simplest solution would be provided if SiF_4 rather than TiF_4 evaporated when the sample was fumed with hydrogen fluoride. To this end he produced TiF_4 (which until then had been unknown) from TiCl_4 and anhydrous hydrogen fluoride. The TiF_4 produced only sublimed at 300°C whereas TiCl_4 boils at 136°C . Such unusual properties of fluorine compounds fascinated Ruff so much that it was to remain his favourite area up to the end of his life in 1939. Ruff could have obtained TiF_4 from Ti and F_2 but, as he wrote in 1907, elementary fluorine is difficult and costly to prepare, so that the preparation of larger quantities of fluorides in this way would be impossible. He therefore first tried to prepare fluorides from chlorides with anhydrous hydrogen fluoride. This is an excellent method which led to the production of SnF_4 , SbF_5 (1904), SOF_2 from nitrogen sulphide (1905), WF_6 from WCl_6 and AsF_3 , as well as WO_2F_2 , WOCl_4 , MoO_2F_2 and MoOF_4 (1907). This topic is referred to in greater detail below.

Elementary fluorine

Chemical preparation

Attempts at producing fluorine chemically were initially made in the 19th century and were continued in the 20th century, but without success. References in the literature to an F_2 emission upon heating AgF_2 , CoF_3 , MnF_3 , PbF_4 , CeF_4 and BiF_5 have been shown to be erroneous. The preparation of all these compounds requires elementary fluorine. AgF_2 has a dissociation pressure <0.1 atm at 700°C , like MnF_3 and CoF_3 at 600°C while PbF_4 , CeF_4 and BiF_5 are stable even when red hot (von Wartenberg; 1939, 1940). Compounds resulting from the elements or from the reaction of fluorides with fluorine must, of course, be excluded as preparative sources of fluorine itself.

Electrochemical preparation

The electrochemical preparation of elementary fluorine, as described by Moissan, is essentially the basis for all subsequent procedures, including modern methods, which are reviewed in Chapter 6. However, the materials employed for the containers and the electrodes, and the electrolyte composition have all been changed during the course of time.

Moissan himself replaced the Pt/Ir U tube originally employed as the reaction vessel with a Cu tube in order to eliminate the loss of platinum. With a few improvements, this equipment was used by Ruff (1899) until *ca.* 1920 and generated 3 litres of F_2 per hour. Subsequently, the Cu tube was replaced by a copper receptacle for the electrolyte which simultaneously acted as a cathode. The copper cover which contained the hollow, cooled Pt anode and a diaphragm made of copper was insulated from the copper cathode (Société Poulenc frères, Meslans; 1900).

The use of molten KHF_2 at a temperature of $240 - 280^\circ\text{C}$ and the replacement of the Pt anode by one of graphite (Argo, Mathers, Humiston and Anderson; 1919) was an important improvement. Simons (1920), Ruff

(1920, 1934) and others used these and comparable cells. Various other materials have also been suggested for the vessels, for example, Monel metal (Schumb and Gamble; 1930), nickel (Miller and Bigelow; 1936), magnesium (Bancroft and Jones; 1929) and graphite (Meyer and Sandow; 1920). Graphite has been used both as an anode and a cathode (Dennis, Veeder and Rochow; 1931; Henne; 1938). Bodenstein, Jockusch and Krekeler (1935) used Electron as the material for their vessels and silver for their cathodes. Molten $\text{KF} \cdot 1.8\text{HF}$ (at a temperature of 160 - 250 °C) was shown to have distinct advantages, as a high HF content corrodes the graphite anodes (Fredenhagen and Krefft; 1929). The occurrence of carbon fluorides, which are difficult to remove, has been found to be a disadvantage as far as the use of graphite electrodes is concerned. In addition, a layer of polymeric $(\text{CF})_x$ is formed on the anode during longer periods of electrolysis, with the result that the bath potential is increased to an undesirable level. The nature of $(\text{CF})_x$, first discovered and characterised by Ruff, is dealt with below. These disadvantages may be avoided by using the procedure adopted by Lebeau and Damiens (1925), who employed $\text{KF} \cdot 3\text{HF}$ which has a melting point of 65 °C as the electrolyte, together with a nickel anode and a copper vessel (cathode). A similar cell was described by Cady (1939) who used a Monel vessel as the cathode and, in a somewhat modified form, by von Wartenberg (1940). The present author obtained very good results with this equipment over a number of years.

A further complication emerged during the electrolysis itself. Liquid hydrogen fluoride, and indeed every combination of molten liquid potassium fluoride, is strongly hygroscopic, the resulting moist electrolyte producing impurities such as O_2 , O_3 and, as later discovered, OF_2 . For this reason it is important to work with electrolytes free of water with the equipment being sealed externally, in the same way as the electrodes have to be sealed internally. Examples of materials which have been used for sealing include solidified electrolytes, fluorite, sealing wax, red lead and glycerine, Portland cement, Bakelite cement and aluminium fluoride. Fluorinated products derived from caoutchouc have been suggested for equipment using $\text{KF} \cdot 3\text{HF}$ as the electrolyte because of its low melting point (IG Farben Industrie AG, Ger. Pat. 671 460, 642 883). The hydrogen fluoride contained in the gas generated on electrolysis may be absorbed by passage over NaF when it is converted to NaHF_2 , or alternatively separated by means of a condensation trap.

Dissociation energy

Measurements of the dissociation energy of F_2 were made indirectly between 1922 and 1940, e.g. by extrapolation of the dissociation energies of the other halogens back to F_2 . Such values varied from between 60 to 81 kcal mol⁻¹ and, as later discovered, were far too high. Schmitz and Schumacher were the first to indicate somewhat lower values for $D(\text{F}_2)$ of 33.4 or 30.6 kcal mol⁻¹, their results being published in 1947 although the measurements were made before 1945. The optimum value accepted nowadays is 36.95 kcal mol⁻¹ [8].

Hydrogen fluoride

Hydrogen fluoride was obtained from the reaction between fluorspar and concentrated sulphuric acid over 200 years ago, although cryolite was later used as a starting material. The resulting acid contains impurities, particularly water but also HSO_3F . Pure hydrogen fluoride may be obtained by heating anhydrous KHF_2 , although the latter must be carefully dried (Ruff; 1920). However, the best method of drying is electrolysis (Simons; 1931). Anhydrous hydrofluoric acid may be stored in Pt or Cu vessels.

The boiling point of HF (19.5 °C) and the dielectric constant (83.6 °C) are relatively high in comparison with the other hydrogen halides and indicates the association of HF molecules in the liquid state (Mallet; 1881; Thorpe and Hambly; 1888, 1889). From steam pressure and steam density measurements, Simons and Hildebrand (1924) postulated that the equilibrium $6 \text{ HF} \rightleftharpoons (\text{HF})_6$ exists in the gaseous state, with the latter species having a ring structure and containing ionic FHF hydrogen bridges. This species was also assumed by Long, Hildebrand and Morell (1943). In contrast, Fredenhagen (1934) presumed the existence of linear polymers of the type $(\text{HF})_2$, $(\text{HF})_3$, etc. and Briegleb (1941 - 3) suggested the presence of an equilibrium of the form $\text{HF} + (\text{HF})_{n-1} \rightleftharpoons (\text{HF})_n$, where $n = 2, 3, 4$, etc. This view was supported by the fact that zigzag $\text{FH} \cdots \text{F}$ chains, connected by hydrogen bonds, may be identified by electron diffraction in the gaseous state (Bauer, Beach and Simons; 1939: $d(\text{FHF}) = 2.55 \text{ \AA}$; $\angle \text{HFH} \text{ ca. } 140^\circ$) and by X-ray diffraction in the solid state (Guenther, Hohn and Strunz; 1939: $d(\text{FHF}) = 2.7 \text{ \AA}$; $\angle \text{HFH } 134^\circ$). These two seemingly contradictory viewpoints of the structure of polymeric HF molecules in the gaseous state — rings or chains — are still being actively discussed at present (see Gmelin's work [8]). Little is known about HF polymers in the liquid state, but the existence of chains connected by hydrogen bonds has been suggested and is still presumed today (*cf.* Bernal; 1933).

Hydrogen fluoride as a solvent

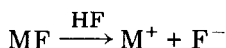
Since hydrogen fluoride is extremely reactive, special materials are necessary for its handling and storage. It has long been known that glass is corroded by HF with the formation of SiF_4 . Platinum is suitable but expensive. For this reason, paraffin hydrocarbons and caoutchouc have often been used and, in 1936, Ruff suggested the use of vessels made out of silver, copper or steel. Of considerable importance in his studies of hydrogen fluoride as a solvent was Fredenhagen's observation (1931) that quartz is not corroded by hydrogen fluoride.

It was presumed that hydrogen fluoride's high dielectric constant would endow it with excellent properties as a solvent. Although this proved to be true, quantitative details regarding the solubility of materials in HF are, however, sparse and often contradictory.

Pure liquid hydrogen fluoride is poorly dissociated and has a low conductance. On the other hand, solutions of a large number of inorganic and organic compounds are characterised by good electric conductivity,

often better than aqueous solutions of the same compounds at the same concentration. Measurements of the boiling point elevation and conductivities made by Fredenhagen and coworkers (1930 - 9) give an insight into the types of reactions occurring in HF solutions. Conclusions have been drawn from these measurements as to the number of charged or uncharged particles in solution, although these methods do not allow any predictions regarding the nature of these particles. The results of the work conducted by Fredenhagen were still used after 1945 but nowadays better results can be obtained from spectroscopic methods, especially NMR spectroscopy. For example, conductivity measurements led to the belief that the HNO_3 molecule formed in a KNO_3/HF solution was protonated to yield H_2NO_3^+ (Fredenhagen and Cadenbach; 1930). Experiments undertaken by del Greco and Gryder (1961) using Raman and IR spectroscopy indicate, however, the presence of NO_2^+ ions in dilute solutions and of undissociated HNO_3 molecules in concentrated solutions.

Solutions of the alkali metal fluorides, which are more soluble in hydrogen fluoride than the alkaline earth fluorides, were first discussed on the basis of solvations of the type:



However such fluorides must be considered as the simplest Lewis bases in the hydrogen fluoride system since $\text{MF} + \text{HF} \rightarrow \text{M}^+ + \text{HF}_2^-$, *i.e.* what occurs in solution is not a simple ionisation but solvolysis. A strong FHF hydrogen bond exists in the HF_2^- ion. According to Fredenhagen, Cadenbach and Klatt (1933) and Klatt (1935 - 7), a large number of organic acids, alcohols, aldehydes, ethers and amines act as bases when dissolved in hydrogen fluoride and are protonated. The observed behaviour of hydrogen fluoride in this connection as a very strong Brönsted acid has led to the concept of super acids; one such acid is a mixture of hydrogen fluoride and SbF_5 (Hyman *et al.*; 1961. Gillespie *et al.*; 1966). At first it was difficult to explain the very much lower acidity of aqueous solutions of hydrogen fluoride in comparison to those of the other hydrogen halides. The reduced proton mobility resulting from hydrogen bonding between F^- ions, HF and H_2O (or H_3O^+) explains this behaviour, however. It is interesting to note that neither H_2O nor NH_3 is readily soluble in anhydrous hydrogen fluoride. Carbonates dissolve with the evolution of CO_2 ; chlorides, bromides and iodides react with the release of the respective hydrogen halide, which is not soluble in hydrogen fluoride. That explains why this reaction, which was often used by Ruff, is so suitable for the preparation of the corresponding anhydrous fluorides.

Hydrogen fluoride has become one of the most important of all fluorine compounds. Not only does it serve in the preparation of many inorganic fluorides, as mentioned above, but also in the fluorination of organic compounds. It has also proved useful as a catalyst for alkylations and acylations as well as for polymerisation processes (Simons; 1940).

Analytical chemistry of fluorine and of fluorine compounds

Although great difficulties were encountered in the preparation of fluorine and many of its compounds, the analytical determination of fluorine proved to be even more difficult and complicated. Thus Yost and Hatcher wrote in 1933 that "a completely satisfactory procedure for the determination of fluorine has never been found" and as recently as 1973 O'Donald complained that "the literature of inorganic fluorine chemistry is bedevilled by the general unreliability of quoted analyses". The development of gravimetric, volumetric, gasometric, colorimetric, potentiometric and conductimetric procedures for analysis are not described here — a summary of the methods known up to 1920 can be found in Ruff [14], while those up to 1933 have been described by Yost and Hatcher; see also Gmelin [8]. Through the use of modern methods, e.g. complexometric titrations and the use of ion-specific electrodes, the fluoride ion may be determined rapidly and reasonably accurately.

Fluorination reagents

As Ruff observed in 1907, reactions with elementary fluorine are both difficult and costly. It was soon established, however, that elementary fluorine is not necessary for most fluorination reactions. The special section of this chapter below considers those situations where elementary fluorine must be employed, e.g. with higher metals or different non-metal fluorides. In fact many metal fluorides were known (see Table 3.1) before elementary fluorine had been isolated. Ruff (1904 - 7) found that most chlorides, bromides and iodides of Groups IV, V and VI in the Periodic Table could be transformed into fluorides through treatment with liquid hydrogen fluoride or gaseous hydrogen fluoride (Chauvenet; 1908). Many lower metal fluorides may be prepared from the appropriate carbonates, oxides or hydroxides through reactions with aqueous hydrofluoric acid (Ruff; 1920). In this way alkali fluorides were readily obtained, as were PbF_2 , SbF_3 , AsF_3 and Hg_2F_2 . Fluorides also resulted from hydrogen fluoride adducts. Particularly noteworthy is SbF_3 [with a little SbCl_5 added as a catalyst (Swarts)] which has proved suitable not only for the fluorination of organic compounds but also a number of inorganic compounds. This method can also be used for the production of mixed halides (Maddock, Emeléus and Reid; 1939; Booth; 1940). Further reactions involving metal fluorides such as PbF_2 , ZnF_2 , CoF_3 , AgF , AgF_2 and others are presented below.

Materials used in fluorination reactions

Ruff described the materials used in fluorination reactions up to 1920 in his book published in that year, and further details are given in the special section below under the individual fluorides. It was realised early that dry fluorine does not corrode glass or quartz, while nickel or copper, which are covered by a protective layer of fluoride during use, are useful for higher temperatures. Platinum, which was often used in the early years of this century, starts to corrode at temperatures as low as 400 °C. Furthermore,

although appliances made of fluorite (CaF_2) are satisfactory for use with elementary fluorine (Ruff and Riebeck; 1928, 1929), boats, pipes etc. made of sintered alumina as recommended by Klemm and Henkel (1934) are better and much easier to use and are only significantly corroded by F_2 above 650°C (von Wartenberg; 1940).

Special considerations

The binary fluorides of the elements which had been established by 1945 are set out in Table 3.1. Those species known in 1900 are printed in italics, those discovered by Ruff are printed in bold lettering and the remaining fluorides are printed normally. Structures determined up to 1945 are indicated with an asterisk. Modern aspects of Main Group fluorides are considered by Shreeve (Chapter 9) and of transition metal fluorides by Winfield (Chapter 8).

Non-metal fluorides

Halogen fluorides

Inexplicable explosions, which occurred while using chlorine-fluorine mixtures for the fluorination of uranium and the platinum metals, led Ruff and his coworkers to the discovery of chlorine monofluoride ClF in 1928; this marked the start of Ruff's successful research on halogen fluorides.

TABLE 3.1

Binary fluorides

A. Fluorides of the Main Group elements

IA:	<i>LiF</i> *, <i>NaF</i> *, <i>KF</i> *, <i>RbF</i> *, <i>CsF</i> *
IIA:	<i>BeF</i> ₂ *, <i>MgF</i> ₂ *, <i>CaF</i> ₂ *, <i>SrF</i> ₂ *, <i>BaF</i> ₂ *
IIIA:	<i>BF</i> ₃ *, <i>AlF</i> ₃ *, <i>AlF</i> , <i>GaF</i> ₃ , <i>InF</i> ₃ , <i>TlF</i> ₃ , <i>TlF</i> *
IVA:	<i>CF</i> ₄ *, (<i>CF</i>) _x *, <i>SiF</i> ₄ *, <i>Si</i> ₂ <i>F</i> ₆ , <i>GeF</i> ₄ , <i>GeF</i> ₂ , <i>SnF</i> ₄ , <i>SnF</i> ₂ , <i>PbF</i> ₄ , <i>PbF</i> ₂ *
VA:	<i>NF</i> ₃ *, <i>PF</i> ₃ *, <i>PF</i> ₅ *, <i>AsF</i> ₃ *, <i>AsF</i> ₅ , <i>SbF</i> ₃ *, <i>SbF</i> ₅ , <i>BiF</i> ₃ *, <i>BiF</i> ₅
VIA:	<i>OF</i> ₂ *, <i>O</i> ₂ <i>F</i> ₂ , <i>SF</i> ₆ *, <i>S</i> ₂ <i>F</i> ₁₀ , <i>SF</i> ₄ , <i>SeF</i> ₆ *, <i>SeF</i> ₄ , <i>TeF</i> ₆ *
VIIA:	<i>ClF</i> , <i>ClF</i> ₃ , <i>BrF</i> , <i>BrF</i> ₃ , <i>BrF</i> ₅ , <i>IF</i> ₅ , <i>IF</i> ₇

B. Fluorides of the transition elements

IB:	<i>CuF</i> ₂ , (<i>CuF</i>), <i>AgF</i> ₂ , <i>AgF</i> *, <i>Ag</i> ₂ <i>F</i> * [†]
IIB:	<i>ZnF</i> ₂ *, <i>CdF</i> ₂ *, <i>HgF</i> ₂ *, <i>Hg</i> ₂ <i>F</i> ₂
IIIB:	<i>ScF</i> ₃ *, <i>YF</i> ₃ *, <i>LaF</i> ₃ *
IVB:	<i>TiF</i> ₄ , <i>ZrF</i> ₄ *, <i>HfF</i> ₄ *
VB:	<i>VF</i> ₃ , <i>VF</i> ₄ , <i>VF</i> ₅ , <i>NbF</i> ₅ , <i>TaF</i> ₅
VIB:	<i>CrF</i> ₅ , <i>CrF</i> ₄ , <i>CrF</i> ₃ , <i>CrF</i> ₂ *, <i>MoF</i> ₆ , <i>WF</i> ₆
VII B:	<i>MnF</i> ₃ , <i>MnF</i> ₂ *, <i>ReF</i> ₆ , <i>ReF</i> ₄
VIII B:	<i>FeF</i> ₃ , <i>FeF</i> ₂ *, <i>CoF</i> ₃ , <i>CoF</i> ₂ , <i>NiF</i> ₂ *, <i>RuF</i> ₅ , <i>RhF</i> ₃ , <i>PdF</i> ₃ , <i>PdF</i> ₂ *, <i>OsF</i> ₆ , (<i>OsF</i> ₄), <i>IrF</i> ₆ , (<i>IrF</i> ₄), <i>PtF</i> ₄

Lanthanoides: *CeF*₄, *CeF*₃*, all further *MF*₃* (and with Eu also *EuF*₂*)

Actinoides: *ThF*₄, *UF*₆, *UF*₄

Subsequently, it became clear that all the halogen fluorides could be synthesised from the elements and that the lower fluorides in particular were exceptionally reactive. Despite this fact, such fluorides could still be prepared in dry equipment made of hard glass and quartz, with the exception of BrF_5 and IF_7 .

Ruff, Ascher, Fischer and Laas (1928) heated a $\text{Cl}_2 + \text{F}_2$ mixture to 250°C in a copper block and found that the mixture ignited and inflamed, and even sometimes exploded. Fractional distillation yielded colourless ClF (m.p., -161°C ; b.p., -103°C), which equalled and sometimes even surpassed fluorine in its reactivity. According to Schmitz and Schumacher (1947), ClF may be derived quantitatively from a mixture of ClF_3 and Cl_2 . Further investigation of reactions involving $\text{Cl}_2 + \text{F}_2$ mixtures led Ruff and Klug (1930) to postulate the equilibrium $\text{ClF} + \text{F}_2 \rightleftharpoons \text{ClF}_3$, which lies towards ClF at 250°C . Colourless ClF_3 (m.p., -83°C ; b.p., 11.3°C) can readily be separated by fractional distillation in copper vessels. It is extremely active with water reacting with a whip-crack noise; it is also capable of inflaming wood.

After Moissan (1900) had failed to obtain pure fluorides by reacting fluorine with bromine, Prideaux (1905, 1906) and Lebeau (1905 - 6) succeeded in producing pure BrF_3 for the first time. Ruff and Menzel (1931) observed an equilibrium between BrF_3 and BrF_5 when the elements were heated in a platinum or copper container. Both compounds were prepared from this equilibrium by fractional condensation. Mainly BrF_5 (m.p., -61.3°C ; b.p., 40.5°C) is formed at 200°C ; in the absence of heat the main product is BrF_3 (m.p., 8.8°C ; b.p., 127°C) (Ruff and Braida; 1932). At 0°C , BrF (m.p., -33°C ; b.p., *ca.* 20°C) results (Ruff; 1933).

Gore (1871) first obtained IF_5 from the reaction of iodine and silver fluoride. Moissan (1891, 1900, 1902) burnt iodine in a stream of fluorine to yield IF_5 . Ruff and Braida (1934) passed a mixture of N_2 and F_2 into a cooled quartz tube over iodine; after fractional distillation IF_5 (m.p., 9.6°C ; b.p., 98°C) was obtained. In this reaction it was found that if the F_2 employed contained O_2 then IOF_3 was also formed. Ruff and Keim (1930) observed the formation of a more volatile substance than IF_5 when raw IF_5 was distilled, and they found that when IF_5 was heated in an F_2 stream IF_7 formed as a colourless gas which does not corrode platinum. At $250 - 70^\circ\text{C}$, 83% of IF_5 transformed into IF_7 (m.p., $5 - 6^\circ\text{C}$; sublimes at 4.5°C).

The halogen fluorides react with all non-metals, except for the noble gases, nitrogen and oxygen; thus, for example, they convert oxides into fluorides. Ruff found that halogen fluorides react explosively with organic substances and that many inorganic compounds either inflame or react briskly with them. From the reaction of ClO_2 with F_2 (diluted with air), Schmitz and Schumacher (1942) isolated chloryl fluoride ClO_2F as a colourless gas (b.p., -6°C) which undergoes ready hydrolysis.

Very little was known about the structures of the halogen fluorides before 1945. From the basis of electron-diffraction measurements, Braune and Pinnow (1937) concluded that IF_5 had a trigonal bipyramidal structure.

The correct structure, which is a square pyramid, was predicted by Wells (1945) [20]. Remarkably the only known oxyfluoride of iodine is KIO_2F_2 obtained by the action of hydrofluoric acid and potassium iodate. An electron pair exists in the equatorial position in the trigonal pyramidal structure of this compound (Helmholtz and Rogers; 1940).

Oxygen fluorides

It was a great disappointment to Ruff when Lebeau and Damiens (1927, 1929) synthesised OF_2 for the first time by passing a stream of fluorine into a 2% solution of sodium hydroxide by means of a platinum tube held directly below the surface of the liquid. Both Ruff and Zedner (1909) and Gallo (1910) had previously attempted to isolate this material without success. OF_2 (m.p., -223.8°C ; b.p., -146.5°C) does not corrode glass and is therefore readily purified and employed. Other authors have also studied OF_2 , for example Ruff and Menzel (1931), Dennis and Rochow (1933), and Cady (1935). OF_2 hydrolyses according to the equation $\text{OF}_2 + \text{H}_2\text{O} \rightarrow \text{O}_2 + 2\text{HF}$, thus acting as a powerful oxidising agent in aqueous solution where it is capable of converting Mn^{2+} to MnO_4^- and Pb^{2+} to PbO_2 . Its structure has been determined both by electron diffraction and IR techniques ($\angle\text{FOF } 104^\circ$; $d(\text{OF}) = 1.36 \text{ \AA}$) (Boersch; 1935; Sutton and Brockway; 1935; Sutherland and Penney; 1936).

Ruff and Menzel (1933) had, however, the satisfaction of discovering a new oxygen fluoride a few years later, when they isolated the unstable O_2F_2 (m.p., -163.5°C), which occurs when an equimolar mixture of O_2 and F_2 is subjected to an electrical discharge in a quartz chamber at 15 - 20 Torr pressure. O_2F_2 is stable only up to -40°C . The decomposition of $\text{O}_2 + \text{F}_2$ is unimolecular and homogeneous (Frisch and Schumacher; 1936, 1937). More recent research has concluded that O_3F_2 (Aoyama and Sakurata; 1938) is probably a mixture of O_4F_2 and O_2F_2 (see Shreeve, Chapter 9).

Dennis and Rochow (1932) reported the isolation of HFO_3 or AgFO_3 , or alternatively HOF , but this was seriously doubted by Cady (1934) and Ruff (1936). The first oxo acid of fluorine (HOF) was prepared and characterised in 1971 by Studier and Appelmann.

*Sulphur, selenium and tellurium fluorides**

Moissan and Lebeau (1900) burnt sulphur, selenium and tellurium in fluorine gas and isolated substances which they then formulated as SF_6 , SeF_6 and TeF_6 . Pure fluorides were not obtained, however. Indeed the purest sample of SF_6 was obtained by Schumb and Gamble in 1930 (m.p., -50.8°C ; sublimes at -63.8°C), and Prideaux (1906) succeeded in preparing pure SeF_6 and TeF_6 by reaction of the elements in a copper tube (SeF_6 : triple pt., -34.7°C ; b.p., -45.9°C . TeF_6 : triple pt., -37.7°C ; b.p., -38.4°C) (cf. Klemm and Henkel; 1932, 1933). The inert behaviour of SF_6 is particularly striking. It does not decompose when red hot, nor does it corrode glass nor

*For modern developments in this subject, see Shreeve, Chapter 9.

react with hydrogen or oxygen, and it only reacts with water at high temperatures. SeF_6 is more reactive than SF_6 , *i.e.* when combined with NH_3 at 200°C it yields N_2 , Se and hydrogen fluoride; and TeF_6 is more reactive than SeF_6 — it hydrolyses to $\text{Te}(\text{OH})_6$ within 24 h whereas SeF_6 is hardly attacked at all over an equivalent period of time (Prideaux; 1906). All hexafluorides have regular octahedral structures (Braune and Knoke; 1933; Brockway and Pauling; 1933). SF_6 was suggested as an insulating atmosphere for high voltage equipment because of its kinetically inert character (Brüchner *et al.*; 1946). Careful separation of the gaseous mixture obtained from the reaction of sulphur with fluorine enabled the extraction of traces of S_2F_{10} (Denbigh and Whytlaw-Gray; 1934) but the material was only prepared in bulk after 1945. It proved to be extremely poisonous.

Lower fluorides — SF_4 may be prepared from sulphur and CoF_3 on heating (Fischer and Jaenckner; 1929). The colourless gas (m.p., -124°C ; b.p., -40°C) does not react with glass or rubber and is easily hydrolysed. SeF_4 (m.p., -13.2°C) was prepared in a pure form by Prideaux and Cox in 1928 from SeCl_4 and silver fluoride, Lebeau having already obtained the impure material in 1907. TeF_4 forms when Te and TeF_6 are heated in an aluminium oxide tube (Hartley, Henry and Whytlaw-Gray; 1938). Centnerszwer and Strenk (1923, 1925) and Trautz and Ehrmann (1935) obtained impure lower fluorides from the reactions of sulphur with AgF . Both S_2F_2 and SF_2 were prepared in a pure form after 1945 (Seel and Gölitz; 1964; Glemser, Heussner and Haas; 1965).

A number of sulphur oxyfluorides have also been prepared. Thus thionyl fluoride, SOF_2 (m.p., -110.5°C ; b.p., -43.7°C), is obtained from SOCl_2 and ZnF_2 (Meslans; 1896), $\text{S}_4\text{N}_4 + \text{CuO} + \text{HF}$ (Ruff and Thiel; 1905), SOCl_2 and SbF_3 (Booth and Mericola; 1940) or by passing HF into a mixture of SOCl_2 and SbCl_5 (*FIAT Review* [7]). It has a pyramidal structure (Yost; 1938; Stevenson and Cooley; 1940). The colourless gas SO_2F_2 forms from $\text{F}_2 + \text{SO}_2$ (Moissan and Lebeau; 1901), although the material is best prepared by the decomposition of $\text{Ba}(\text{SO}_3\text{F})_2$; $\text{Ba}(\text{SO}_3\text{F})_2 \rightarrow \text{BaSO}_4 + \text{SO}_2\text{F}_2$ (Traube, Hoerenz and Wunderlich; 1919). SO_2F_2 (m.p., -136.7°C ; b.p., -55.4°C) has a tetrahedral structure [$d(\text{SO}) = 1.43 \text{ \AA}$, $\angle \text{OSF } 105^\circ$, $\angle \text{FSF } 100^\circ$ (Stevenson and Russell; 1939)]. SOF_2 smells like partially hydrolysed phosgene, whereas SO_2F_2 is odourless and inert to water. SOF_4 (m.p., -107°C ; b.p., -48.5°C) is obtained from the reaction of SOF_2 and F_2 at 150°C (*FIAT Review* [7]). Other oxyfluorides such as SOCIF and SO_2CIF were described before 1945. Fluorosulphuric acid HSO_3F is obtained either by reaction of fuming sulphuric acid with KHF_2 (Meyer and Schramm; 1932) or SO_3 with hydrofluoric acid [*Ger. Pat. 52953*(1935)]. The compound hydrolyses slowly in the presence of water and is the basis of super acids nowadays.

Nitrogen fluorides

Like Ruff and Geisel (1903), Moissan (1891) had tried in vain to produce nitrogen-fluorine compounds. After many further attempts, Ruff, Fischer and Luft (1928) finally succeeded in preparing the colourless gas

NF_3 (m.p., -208°C ; b.p., -129°C) by the electrolysis of molten anhydrous NH_4HF_2 at *ca.* 125°C in a copper bell (which was used as a cathode) employing a graphite rod as the anode. The material possesses a pyramidal structure [$\angle \text{FNF } 110^\circ$; $d(\text{NF}) = 1.45 \text{ \AA}$ (Bailey, Hale and Thompson; 1937)]. NF_3 is virtually insoluble in water and in KOH solution, and it does not corrode either glass or mercury. It is thus quite stable unlike the explosive NCl_3 . In contrast to SF_6 , NF_3 reacts with alkali metals. It is inert towards H_2 at 350°C , but the mixture explodes when sparked.

Small quantities of NHF_2 and NH_2F are formed as by-products of the electrolysis (Ruff and Staub; 1931). The presence of NH_2F ; as well as NF_2 described further on (perhaps impure OF_2 ?) could not be substantiated. NHF_2 is extremely reactive and explosive; its true nature was only established after 1945. If fluorine, diluted with nitrogen, is allowed to react with HN_3 , a yellow green gas is generated. This was formulated as N_3F (m.p., -154°C). It is converted to N_2F_2 (m.p., -110°C) under 200 Torr pressure. N_2F_2 exists as a *cis/trans* isomeric mixture (Haller; 1942), the structure of both isomers having been determined by Bauer in 1947 through the use of electron-diffraction methods.

Nitrogen oxyfluorides — Moissan and Lebeau isolated the first nitrogen oxyfluoride NO_2F (m.p., -166.5°C ; b.p., -72.4°C) by burning NO in F_2 . NO_2F may also be obtained from the reaction of NO_2 and F_2 (Ruff, Menzel and Neumann; 1932). It hydrolyses to nitric and hydrofluoric acids, and acts as a strong oxidising and fluorinating agent.

When NOCl is passed over AgF in a platinum tube at $200 - 50^\circ\text{C}$, NOF (m.p., -132.5°C ; b.p., -59.9°C) is obtained (Ruff and Stäuber; 1905). This compound also results from the reaction of NO and fluorine (Ruff, Menzel and Neumann; 1932). NOF attacks various elements in the same way as NO_2F , but not quite so strongly. On melting with OF_2 , NF_3 is formed (Ruff, Menzel and Neumann; 1932). Reaction with AsF_5 and SbF_5 leads to the formation of $\text{NO}(\text{AsF}_6)$ and $\text{NO}(\text{SbF}_6)$ respectively [this formulation being advanced by Asmussen in 1940; Ruff formulated them as $\text{NOF} \cdot \text{AsF}_5$ in 1907]. In the presence of water, NOF yields nitric acid and hydrogen fluoride.

Moissan observed in 1891 that the reaction of F_2 with HNO_3 led to explosions. Cady (1934) investigated the reaction further and was able to obtain NO_3F from a dilute solution of HNO_3 and F_2 . Almost simultaneously and independently, Ruff and Kwasnik (1935) prepared this fluoride by reaction of anhydrous nitric acid with fluorine. NO_3F (m.p., -175°C ; b.p., -45.9°C) is a colourless, poisonous gas, stable in dry glass and quartz, but extremely explosive in the gaseous and solid states. NO_3F was the first hypofluorite reported; developments in this area took place quickly after 1945 (Hoffmann; 1964).

Phosphorus fluorides

The compound PF_5 has long been known, Thorpe having obtained it from PCl_5 and AsF_3 in 1876. Because AsF_3 is not easy to handle, other

fluorinating agents have been employed such as PbF_2 or ZnF_2 (Guntz; 1886), for example, or alternatively fluorination of PF_3 with F_2 (Moissan; 1891). PF_5 (m.p., -93.8°C ; b.p., -84.6°C) does not attack dry glass below 250°C . It hydrolyses easily, first to POF_3 and then to H_3PO_4 . Its trigonal bipyramidal structure has been determined by electron diffraction (Brockway and Beach; 1938; Braune and Pinnow; 1937). Hydrofluoric acid or alkali metal fluorides interact with PF_5 to produce PF_6^- ions, which, in contrast to PF_5 , are stable towards water and alkali (Lange; 1930, 1932). The PF_6^- ion is octahedral (Seifert; 1931).

Moissan (1885, 1904) allowed copper phosphide to react with PbF_2 in a brass tube at red heat to give PF_3 . Better results may be achieved by using halogen exchange from PCl_3 to AsF_3 (Moissan; 1885) or alternatively to CaF_2 or SbF_3 (Booth and Bozarth; 1939). PF_3 (m.p., 121.6°C) is much less reactive than PF_5 and has a trigonal pyramidal structure as shown by electron-diffraction studies (Brockway and Pauling; 1935). PF_3 adds halogens, e.g. chlorine, with ease to give PF_3Cl_2 (Moissan; 1885) with apical Cl atoms in the trigonal bipyramid (Brockway and Beach; 1938). Such compounds decompose readily to PF_3 and X_2 . PCl_3 yields PF_2Cl and PFCl_2 with PF_3 ; with Br_2 , PF_3 gives PF_2Br and PFBr_2 (Booth and Frary; 1939).

Phosphorus oxyfluoride, POF_3 — This compound (m.p., -39.8°C ; b.p., -39.4°C) results from the reaction of hydrogen fluoride (Moissan; 1891) and solid fluorides such as cryolite (Thorpe and Humbley; 1889) or CaF_2 (Tarbutton, Egan and Frary; 1941) with P_2O_5 . It hydrolyses to phosphoric acid. The corresponding sulphur compound PSF_3 can be obtained from the reactions of P_2S_5 with PbF_2 or BiF_3 , or from halogen exchange reactions involving PSCl_3 and AsF_3 (Thorpe and Rodger; 1888, 1889) or ZnF_2 (Moissan; 1890). The PO and PS fluorochlorides, (Booth and Cassidy; 1940) and the fluorobromides (Booth and Seabright; 1943) can be obtained similarly. These compounds are basically tetrahedral (Brockway and Beach; 1938); PSF_3 is similar (Stevenson and Russell; 1939). Phosphoryl and thiophosphoryl fluorides generally behave similarly, hydrolysis giving PO_2F_2^- , PO_3F^- (Lange; 1929) or PSOF_2^- ions (Lange and Askitopoulos; 1938).

The first phosphorus nitride fluoride derivatives (cyclophosphazenes) $\text{P}_4\text{N}_4\text{Cl}_2\text{F}_6$ (m.p., -12°C ; b.p., 105.8°C) and $\text{P}_4\text{N}_4\text{Cl}_4\text{F}_4$ (m.p., -25°C ; b.p., 130.5°C) were obtained by heating $\text{N}_3\text{P}_3\text{Cl}_6$ with PbF_2 (Schmitz-Dumont and Kùlkens; 1938). All of the halides hydrolyse easily. When heated under pressure at 100°C , $\text{P}_4\text{N}_4\text{Cl}_4\text{F}_4$ is transformed into a rubber-like mass which decomposes when heated to $250 - 400^\circ\text{C}$ giving $\text{P}_3\text{N}_3\text{Cl}_2\text{F}_4$ and $\text{P}_3\text{N}_3\text{Cl}_4\text{F}_2$ (Schmitz-Dumont and Braschos; 1939).

Arsenic and antimony fluorides

Moissan (1900) treated AsF_3 with fluorine and obtained a fuming gas. The first pure AsF_5 (m.p., -80°C ; b.p., -53°C) was produced by Ruff and Graf (1906) from the trifluoride and SbF_5 in the presence of bromine. Arsenic can also be converted to the pentafluoride with fluorine (Ruff,

Braida, Bretschneider, Menzel and Plaut; 1932). Like PF_5 , AsF_5 is hydrolytically unstable and with NOF yields $\text{NO}(\text{AsF}_6)$. The AsF_6^- ion in KAsF_6 is hydrolysed more readily than the PF_6^- ion. AsF_3 (m.p., -5.95°C ; b.p., 62.8°C) is easily produced by heating the trioxide with CaF_2 and sulphuric acid (Moissan; 1884; Ruff; 1920 [11]; Russell, Rundle and Yost; 1941). It has a pyramidal structure according to electron-diffraction measurements (Pauling and Brockway; 1935) and from Raman spectra (Yost and Sherborne; 1934). It hydrolyses readily and forms KAsF_4 with potassium fluoride.

The reaction of antimony pentachloride with anhydrous hydrogen fluoride provides a good method of preparing SbF_5 (m.p., 7°C ; b.p., 150°C) (Ruff, Graf, Heller and Knoch; 1906). The reaction of antimony with fluorine, as used by Moissan, does not yield a pure product. Treatment of SbF_5 with NaOH solutions leads to hydrolysis and the generation of $\text{Sb}(\text{OH})_6^-$ ions, while $\text{NO}(\text{SbF}_6)$ forms with NOF (Ruff, Stäuber and Graf; 1906) and MSbF_6 with alkali fluorides. These contain octahedral SbF_6^- ions (cf. also Lange and Askitopoulos; 1935). Addition compounds arising from the strong Lewis acidity of SbF_6^- result with SO_2 , for example. The nature of the addition compounds of AsF_5 and SbF_5 with halogens or sulphur, e.g. $\text{SbF}_5 \cdot \text{Br}$, $\text{SbF}_5 \cdot \text{I}$, $\text{AsF}_5 \cdot \text{S}$ and $\text{SbF}_5 \cdot \text{S}$ (Ruff, Graf, Heller and Knoch; 1906), has only been explained recently. Polycations are present in the halogens, simple MF_6^- ions or the corresponding polyanions involving arsenic or antimony. SbF_5 is a good fluorinating agent. Mixed fluorine-chlorine compounds, e.g. $\text{SbCl}_5 \cdot \text{SbF}_3$, $\text{SbCl}_5 \cdot \text{SbF}_5$ and SbCl_3F_2 are also known (Ruff, Zedner, Knoch and Graf; 1909).

Swarts (1892) prepared pure antimony trifluoride SbF_3 by dissolving Sb_2O_3 in hydrofluoric acid and then removing water. The combination of SbCl_3 with hydrogen fluoride also provides a good method of preparation (Biltz and Rahlfs; 1927). SbF_3 (m.p., 292°C ; b.p., 319°C) has the same pyramidal structure as AsF_3 (Byström and Westgren; 1943). It is soluble in water, with a limited hydrolysis whose extent was not studied during the timespan covered by this chapter. SbOF , which has often been described, has not been confirmed to date. Complexes such as KSbF_4 , K_2SbF_5 , Na_3SbF_6 and $\text{TiSb}_3\text{F}_{10}$ are formed with alkali metal fluorides. The structures of these compounds are not known and their formulae cannot always be established. SbF_3 is an excellent fluorinating agent, as already mentioned above. SbF_3Cl_2 is used as a catalyst in the Swarts reaction or directly as a fluorinating agent (Henne and Trott; 1947). Ruff and Plato (1904) synthesised a number of antimony(III, V) fluorides, e.g. $5\text{SbF}_3 \cdot \text{SbF}_5$ or $2\text{SbF}_3 \cdot \text{SbF}_5$ (?).

Carbon fluorides

The present chapter does not deal with CF_4 , which Lebeau and Damiens (1926) first isolated and which Ruff and Keim (1930) fully characterised. The polymer $(\text{CF})_x$ is of current great technical interest. It forms as an undesired product on graphite electrodes during the electrolytic production of F_2 (Ruff; 1933). Ruff and Bretschneider (1934) also obtained it from the reaction of graphite and F_2 at 420°C . Debye-Scherrer photographs led the

authors to assume that the F^- ions in $(CF)_x$ are intercalated between the carbon layers in the graphite structure by expansion of these layers from 3.35 Å to 8.17 Å. Rüdorff and Rüdorff (1947) [7] suggested the existence of a covalent bond between the F atoms and each carbon atom, which is now tetrahedrally bonded as a result of the carbon layers being buckled. By heating $(CF)_x$ at higher temperatures, carbon fluoride homologues may be formed (Ruff and Bretschneider; 1933).

Silicon and germanium fluorides

Silicon tetrafluoride, SiF_4 , discovered by Scheele in 1774, is always formed when silicic acid or its salts react with hydrogen fluoride. The sublimation point of SiF_4 is $-95.1^\circ C$, and it has a tetrahedral structure with $d(SiF) = 1.54$ Å (Brockway and Wall; 1934). SiF_4 is very stable thermally. Silicic acid and SiF_6^{2-} ions are formed by hydrolysis. SiF_4 and hydrogen fluoride do not react together. Fluorosilicates possess the octahedral ion SiF_6^{2-} . Sodium, potassium and barium salts are relatively insoluble. On combination with $SiCl_4$ in glass at $600^\circ C$, SiF_4 gives SiF_3Cl , SiF_2Cl_2 and $SiFCl_3$ (Hill, Lindsay and Wiley; 1946). These fluorides can also be obtained from the reaction of $SiCl_4$ with SbF_3 (Booth and Swinehart; 1935).

The fluorosilanes $HSiF_3$ and H_2SiF_2 are obtained from the appropriate chlorides by reaction with SbF_3 (Booth and Stillwell; 1934; Emeléus and Maddock, 1944). Ruff and Albert (1905) synthesised $HSiF_3$ by treatment of $HSiCl_3$ with TiF_4 . This was the first compound of its class to be isolated. The readily hydrolysable compounds $Si_2OF_3Cl_3$, $Si_2OF_4Cl_2$ and Si_2OF_6 (Booth and Osten; 1945) form when Si_2OCl_6 is fluorinated with SbF_3 . Si_2F_6 (triple pt., $18.7^\circ C$) may be obtained from the appropriate chloride by reaction with ZnF_2 (Schumb and Gamble; 1931, 1932). More recent work has shown that subfluorides may be obtained from SiF_4 and Si as well as many higher homologues of SiF_4 .

GeF_4 (sublimes at $-35^\circ C$) was first prepared by the thermal decomposition of $BaGeF_6$ at $750^\circ C$ in a quartz tube (Dennis and Laubengayer; 1927; Biltz, Le Boucher and Fischer; 1932). It readily hydrolyses in a similar manner to SiF_4 , forming germanic acids and GeF_6^{2-} ions. If the clear solution is treated with KOH, K_2GeF_6 results [containing an octahedral GeF_6^{2-} ion (Hoard and Vincent; 1939)]. GeF_2 is formed when GeF_4 is passed over germanium powder at $100^\circ C$. This sublimes at $220^\circ C$, and yields Ge and GeF_4 at higher temperatures. It displays strong reducing properties (Dennis and Laubengayer; 1927).

Boron trifluoride

In keeping with its importance, many methods for synthesising boron trifluoride were developed from an early date. Heating NaF or $NaBF_4$ with B_2O_3 and sulphuric acid (Booth and Wilson; 1935) was a commonly used method which can be traced back to Davy, who used fluorite as a source of fluorine (1812, 1813). However, CaF_2 yields a solid residue after reaction, which cannot be removed without breaking the flask; this can be avoided by

using NaF or NaBF₄. The same results are obtained with cryolite (Ruff; 1920 [14]). The halogen exchange of BCl₃ with F₂ (Moissan; 1891) and silver fluoride (Ruff; 1920; Pohland and Harlos; 1932) or SbF₃ (Booth and Frary; 1943) has also been carried out. Thermal treatment of tetrafluoroborates generates BF₃ [de Boer and van Liempt; 1927; Loder, *U.S. Pat. 2 135 460*(1938)]. In its pure form BF₃ can be elegantly produced by the thermal decomposition of diazonium fluoroborates according to the equation $\text{ArN}_2\text{BF}_4 \rightarrow \text{ArF} + \text{N}_2 + \text{BF}_3$ (Balz and Schiemann; 1927).

BF₃ (m.p., -127.1 °C; b.p., -101.0 °C) has a planar structure with $d(\text{BF}) = 1.30 \text{ \AA}$ (Levy and Brockway; 1937; Praune and Pinnow; 1937; Laubengayer, Ferguson and Newkirk; 1941). It fumes in air and hydrolyses to boric and fluoroboric acid. BF₃ is very stable thermally and reacts with B₂O₃ to give (BOF)₃ which possesses a ring structure (Baumgarten and Bruns; 1939, 1941), and with AlCl₃ it gives AlF₃ (Gamble, Gilmont and Stiff; 1940). BF₃ is also a strong Lewis acid, and since the F⁻ ions act as donors it reacts with aqueous hydrofluoric acid to give HBF₄. With oxides, hydroxides or carbonates the latter generates salts. BF₃ forms addition compounds with alcohols, aldehydes, ketones, ether and acids where the oxygen atom serves as a donor (Meerwein and Pannwitz; 1934). The etherate (C₂H₅)₂O·BF₃ serves as a catalyst, and BF₃ can be stored in this form. Oxides, hydroxides, sulphates, etc. also give adducts with BF₃, since N, C, P, S or halogen atoms can all serve as donor atoms like the oxygen atoms to form addition compounds [10]. Later work has shown that subfluorides can be obtained from BF₃ and boron.

Attempts to fluorinate the noble gases

Ramsay supplied Moissan with argon and encouraged him to react the gas with fluorine but the attempts were unsuccessful (1895). Ruff and Menzel (1933) subjected mixtures of both argon and fluorine and krypton and fluorine to the influence of electrical discharges in a similar manner to that employed in their attempts to produce O₂F₂ but again obtained only negative results. Antropoff *et al.* (1932, 1933) also failed using similar experiments. However, if these various workers had modified their experimental conditions, they might have discovered krypton difluoride (see Holloway, Chapter 7).

Metal fluorides

Main Group fluorides

In time the general properties of the metal fluorides were also studied from the structural viewpoint. Combining structure with other physical properties such as melting point, boiling point, enthalpy of formation, etc. afforded substantial insights into the nature of the chemical bonding involved. However, workers in the field of fluorine chemistry had to accept the fact that, particularly in the case of fluorides, continuous transitions exist between the various kinds of bonds involved, *i.e.* pure covalent or pure ionic bonds are rare and that, as a rule, bonding lies between these two

extremes. The unusual behaviour of the fluorides as compared with the other halides also became obvious: the fluorides often resemble the corresponding oxides in structure, while the other halogenides are related to the sulphides and the selenides [19]. Gross differences between the fluorides and the other halogenides were also found in chemical properties. Well known examples are: CaF_2 (poorly soluble in water), CaCl_2 (readily soluble), AlF_3 involatile (m.p., 1040°C), AlCl_3 sublimes as Al_2Cl_6 . Knowledge of the structures of these fluorides has helped in understanding all these properties.

Alkali metal fluorides — All the fluorides were known before 1900. They were obtained from the hydroxides or carbonates by reaction with hydrofluoric acid, and all have the NaCl structure. (*Strukturbericht*, Vol. I; 1931 [19]). Variations of these structures from those predicted from radius ratios were recognised and irregularities in melting and boiling points (NaF possesses the maximum) were explained (Pauling; 1940). In contrast, the lattice energies follow the expected trends. Unlike these fluorides, NH_4F crystallises with the wurtzite structure because the NH_4^+ ion forms four tetrahedral NHF bonds with surrounding F^- ions. These, in turn, create tetrahedral NHF^- bonds (Zachariasen and Goldschmidt; 1927). The potassium acid fluorides $\text{KF}\cdot n\text{HF}$, $n = 1 - 3$ were described by Berzelius (1856) and Moissan (1884, 1888).

Alkaline earth metal fluorides — The last of these fluorides, BeF_2 , was obtained in a somewhat impure state by the thermal decomposition of $(\text{NH}_4)\text{BeF}_4$ in a CO_2 stream (Lebeau; 1898). The remaining fluorides were obtained in the usual manner, e.g. by the reaction of oxides, hydroxides or carbonates and hydrofluoric acid. The influence of the radius ratio is clearly noticeable in the structures of the fluorides: BeF_2 crystallises as the β -cristobalite type (Brandenberger; 1932), MgF_2 as the rutile type (*Strukturbericht*, Vol. I; 1931 [19]), while the fluorides of Ca, Sr and Ba possess the CaF_2 structure (*Strukturbericht*, Vol. I; 1931 [19]). The differences between these and the other halogenides are, again, quite large. BeCl_2 sublimes and has discrete BeCl_2 molecules in its crystal lattice in contrast to ionic BeF_2 (m.p., 800°C). While BeF_2 is soluble in water, MgF_2 (like the other alkaline earth metal fluorides) is only sparingly soluble. Increasing solubility from CaF_2 to BaF_2 was understood to be due to an increase in the cation radius resulting in a reduction in the lattice energy. KMgF_3 has a perovskite structure (*Strukturbericht*, Vol. I; 1931 [19]).

Fluorides of the Group III elements — The literature before 1945 describes various ways of producing AlF_3 . Reactions of Al metal with F_2 or hydrogen fluoride at high temperature or of aluminium hydroxide with hydrogen fluoride at $400 - 700^\circ\text{C}$ are, for example, worthy of mention. The thermal decomposition of $(\text{NH}_4)_3\text{AlF}_6$ at red heat (Biltz and Rahlfs; 1927) is quite an acceptable method for preparing AlF_3 (m.p., 1040°C). The structure of this fluoride consists of nearly close packed F^- ions, with the Al^{3+} ions occupying octahedral holes (Ketelaar; 1932). AlF_3 is not very soluble in water, although the AlF_6^{3-} ion (which is present in technically important cryolite) forms in hydrogen fluoride (see Meshri, Chapter 10). The

fluoroaluminates T_2AlF_5 and $TAlF_4$ are interesting. Their structures do not contain any discrete AlF_5^{2-} or AlF_4^- ions but rather AlF_6 octahedra, as in cryolite. In both fluoroaluminates the AlF_6 octahedra are linked in such a way that polymeric AlF_5 chains and polymeric AlF_4 layers are formed (Brosset; 1937/1938). A subfluoride AlF is obtained when Al and AlF_3 are heated at 700 °C (Klemm and Voss; 1943). This subfluoride was discovered because Al metal evaporates in the presence of AlF_3 (Willmore; 1939).

Hannebohm and Klemm (1936) obtained GaF_3 and InF_3 by the decomposition of $(MH_4)_3MF_6$, M = Ga and In, while TlF_3 could be obtained from the oxide and F_2 at 300 °C. While GaF_3 , InF_3 and AlF_3 are not very soluble, TlF_3 is readily decomposed by water. TlF is obtained by reaction of the carbonate or hydroxide with hydrogen fluoride (Ephraim *et al.* and Gewecke; 1909; Ketelaar; 1935; Hayeck; 1935); it possesses a distorted NaCl structure (Ketelaar; 1935).

Fluorides of the Group IV elements — SnF_2 (m.p., 210 - 9 °C) results from the reaction of SnO and hydrogen fluoride in the absence of air; in air $SnOF_2$ is formed (Gay-Lussac and Thénard; 1809). SnF_4 was first produced from tin and F_2 or $SnCl_4$ with hydrogen fluoride by Ruff, Plato and Graf (1904), with an intermediate product, $SnCl_4 \cdot SnF_4$, also being formed, it decomposes at 750 °C. SnF_4 sublimes and is hydrolysed with the formation of $SnO_2(aq.)$ and F^- ions (Wolter; 1912; Furman; 1918). Fluorostannates, M_2SnF_6 , can be produced from SnO_2 , hydrogen fluoride and a metal fluoride. PbF_2 (m.p., 820 - 4 °C), which was known before 1900, may be obtained from the carbonate or hydroxide by reaction with hydrogen fluoride; it occurs in two modifications (Schumann; 1933). It can also be precipitated by hydrogen fluoride from a lead acetate solution (Jellinek and Rudat; 1928). β - PbF_2 possesses the fluorite structure (Kolderup; 1924/5). $PbClF$, which is obtained from $PbCl_2$ and aqueous sodium fluoride solution has a layer structure (Niewenkamp and Bijvoet; 1932). It is employed for the gravimetric determination of lead. PbF_4 (m.p., 600 °C) may be produced from PbF_2 by reaction with F_2 at 300 °C in sintered alumina tubes; it is readily hydrolysed to PbO_2 (von Wartenberg, 1940).

Bismuth fluorides — White BiF_3 (m.p., 725 °C) is produced from $Bi(OH)_3$ and hydrofluoric acid (Muir, Hoffmeister and Robbs; 1881). It can be purified by heating with hydrogen fluoride in a platinum tube at 725 - 30 °C (von Wartenberg; 1940). $BiOF$ has also been described, but it is usually only observed in its impure form. The structure of BiF_3 may be derived from that of fluorite by the addition of F^- ions (Hassel and Nilssen; 1929; Croatto; 1944). BiF_5 , which Ruff was unable to prepare, may be sublimed from BiF_3 in a stream of fluorine at 550 °C. It reacts strongly with water forming ozone and gives BiF_3 with H_2 (von Wartenberg; 1940).

*Transition metal fluorides**

Copper Group fluorides — Pure CuF has not yet been produced, as von Wartenberg pointed out in 1939. On fusion of the impure material, an

*See also Winfield, Chapter 8.

equilibrium is set up between Cu, CuF and CuF₂ with *ca.* 70% CuF present at 900 - 1200 °C. The latter disproportionates to Cu and CuF₂ on cooling. White CuF₂ is obtained from CuCl₂ and fluorine at 400 °C (Ruff and Giese; 1934: Henkel and Klemm; 1935) or, according to earlier observations, from CuO and hydrogen fluoride (von Wartenberg; 1939). CuF₂ is slightly soluble in water with CuO·CuF₂·H₂O believed to be formed (Joly; 1875: Deussen; 1905). The distorted rutile structure for CuF₂ was determined after 1945. Silver forms three fluorides, *i.e.* Ag₂F, AgF and AgF₂. The subfluoride, Ag₂F, which was already mentioned by Guntz (1890) and Wöhler (1912), forms as green crystals when an AgCO₃ + NH₄F solution in 40% hydrofluoric acid is electrolysed at 50 °C using a silver electrode (Hettich; 1927: Scholder and Traulsen; 1931). It decomposes in water and disproportionates to silver and AgF at 100 - 200 °C. The metallic appearance and conductivity of Ag₂F were studied by Brody and Millner (1928). The structure (anti-CdI₂ type) was suggested in 1928 by Terrey and Diamond. Moissan (1891) and Pfaundler (1863) transformed silver carbonate and hydrogen fluoride to yellow AgF (m.p., 435 °C). This is soluble in water, in contrast to the other silver halides. AgF crystallises as the NaCl-type structure as does AgCl (Ott; 1926). Theoretical chemists have been very interested in the solubilities in water of these two compounds and in the low melting point of AgF in comparison to AgCl (m.p., 455 °C). The use of AgF as a fluorinating agent extends back to the beginnings of fluorine chemistry. Black AgF₂ (m.p., 690 °C) is stable up to red heat. It can be prepared from silver leaf (Ebert, Rodowska and Frazer; 1933) or from the reaction of silver halides with fluorine (Ruff and Giese; 1934: von Wartenberg; 1939). AgF₂ dissolves in water producing O₂, and as a strong oxidising agent it converts Mn²⁺ into the permanganate ion. This compound is often described in the pre-1945 literature and even after this date as being a yellow or yellowish brown substance, but such products are low in fluorine content. AgF₂ is also a very good fluorinating agent being comparable with CoF₃ in its effects (von Wartenberg; 1940). No defined gold fluorides were known before 1945.

Zinc Group fluorides — ZnF₂ and CdF₂ are scarcely soluble at all in water, in contrast to the corresponding chlorides. Little was known about the properties of this group prior to 1945. ZnF₂ is derived from ZnCO₃ by reaction with hydrofluoric acid, followed by evaporation and thermal treatment to 300 °C (Ruff; 1920). Zn(OH)F is formed from an NaOH solution (Feitknecht and Bucher; 1943). ZnF₂ (m.p., 734 °C) has the rutile structure (Ferrari; 1926); it has occasionally been used as a mild fluorinating agent. CdF₂ closely resembles ZnF₂ in its preparation and reactions (m.p., *ca.* 1100 °C); it crystallises with the CaF₂ structure (Kolderup; 1924/5). It has been produced from the carbonate and hydrofluoric acid (Klemm, Tilk and von Müllenheim; 1928). Hg₂F₂, obtained from the carbonate by reaction with hydrofluoric acid (Ruff; 1920 [14]), is yellow and blackens in light. It is partially decomposed into HgF₂ and Hg when vaporised. It is more soluble in water than HgCl₂ but undergoes hydrolysis. According to Ruff and Bahlau (1918), HgF₂ is formed either by heating Hg₂F₂ alone or in the

presence of Cl_2 or Br_2 . HgF_2 (m.p., 645°C) has the CaF_2 structure (Ebert and Weitinek; 1933) and is very sensitive to moisture; $\text{Hg}(\text{OH})\text{F}$ has been reported as being formed (Ruff; 1920 [14]). HgF_2 is a mild fluorinating agent, especially for organic compounds. Some complexes, e.g. K_2CdF_4 (Poulenc; 1894), $(\text{NH}_4)_2\text{ZnF}_4$ and $(\text{NH}_4)\text{CdF}_3$ (Kurtenacker, Finger and Hey; 1933), have been reported but their structures have not been determined. KZnF_3 has the perovskite structure (Goldschmidt; 1927).

Scandium Group fluorides — Although Moissan treated the carbides of many of these elements with fluorine, he undertook no further research on the fluorides formed (1896). All the elements form trifluorides MF_3 which are soluble in water. They may be prepared from the oxides, hydroxides or carbonates by reaction with hydrogen fluoride or may be precipitated from chloride or nitrate solutions with hydrofluoric acid. Under these circumstances $\text{MF}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ is formed, yielding anhydrous MF_3 on heating. ScF_3 has the same structure as AlF_3 , while YF_3 is the same as BiF_3 (see later publications on this subject), LaF_3 and other lanthanide trifluorides possess the tysonite structure (Ofstedal; 1929, 1931), and LaOF (obtained by heating $\text{La}_2\text{O}_3 + \text{LaF}_3$ to 900°C) has the fluorite structure like MOF , where $\text{M} = \text{La}$ to Lu and Y (Klemm and Klein; 1941). Of the cerium compounds, CeF_3 and CeF_4 are known. The latter is obtained by heating CeCl_3 and fluorine at 500°C (Klemm and Henkel; 1934) or by heating CeF_3 and fluorine at the same temperature (von Wartenberg; 1940). CeF_4 hydrolyses slowly in water, and is used as a fluorinating agent in organic chemistry. Europium difluoride, EuF_2 , is obtained from the reaction of EuF_3 with hydrogen at 1200°C . It has the fluorite structure (Beck and Nowacki; 1938; Klemm and Döll; 1939).

Titanium Group fluorides — Titanium trifluoride, TiF_3 , was not obtained in the pure state before 1945. TiF_4 (sublimes at 284°C), the first fluorine compound produced by Ruff from TiCl_4 and hydrogen fluoride (Ruff and Ipsen; 1903; Ruff and Plato; 1904), has been mentioned earlier. It forms addition compounds with ammonia, alcohol and pyridine, and fluorotitanates, M_2TiF_6 , with alkali fluorides in the presence of hydrogen fluoride. The structure of TiF_4 is tetrahedral in the gaseous state; it had not been determined in the solid state by 1945. ZrF_4 is obtained in the same way as TiF_4 ; it sublimes at temperatures above 600°C and hydrolyses in water at 50°C (Wolter; 1908). ZrF_4 and HfF_4 have the same structure (Schulze; 1934). The complex $(\text{MH}_4)_3\text{ZrF}_7$ (obtained from ZrO_2 , MH_4F and hydrogen fluoride) is quite interesting. The structure of the ZrF_7^{3-} ion has been described as that of an octahedron distorted by the addition of an F^- ion in the centre of an octahedral plane (Hampson and Pauling; 1938). A more recent evaluation of the structure indicates that it is pentagonal bipyramidal. HfF_4 is produced by the thermal decomposition of $(\text{NH}_4)_2\text{HfF}_6$ in nitrogen at 500°C (Hevesey and Dullenkopf; 1934), while ThF_4 is prepared from reaction of the chloride with fluorine (Moissan and Martiensen; 1905). Complexes of the type M_2ThF_6 ($\text{M} = \text{Pb}, \text{Ca}, \text{Sr}, \text{Ba}$) have the LaF_3 structure [20].

Vanadium Group fluorides — Ruff noted the advantages of fluorination with hydrogen fluoride while producing the vanadium fluorides. Fluorination involving the elements resulted only in small quantities of VF_5 . At 200 °C, VCl_3 gave yellow-green VF_3 (Ruff and Lickfett; 1911) which was almost insoluble in water and sublimed when hot. VCl_4 yielded green, hygroscopic VF_4 , which disproportionated to VF_3 and VF_5 in a Pt tube at 325 °C. VF_5 is colourless and sublimes at 111 °C. It forms VOF_3 in moist air and hydrolyses to V_2O_5 . VO_2 yields VOF_2 when dissolved in hydrogen fluoride and when the latter is vapourised (Ruff and Lickfett; 1911). The structure of the fluorides was not known until after 1945. The literature describes $2\text{NH}_4\text{F}\cdot\text{VF}_3\cdot\text{H}_2\text{O}$ (Petersen; 1889), but this compound is $(\text{NH}_4)_2\text{VF}_5(\text{H}_2\text{O})$ with the K_2PtCl_6 structure (Pirani; 1932).

Niobium and tantalum fluorides — The only fluorides known prior to 1945 were the volatile NbF_5 and TaF_5 , prepared from the elements (Ruff, Zedner, Schiller and Heinzelmann; 1909). The fluorides may also be obtained from the chlorides by reaction with hydrogen fluoride (Ruff and Schiller; 1911). NbF_5 (m.p., 75.5 °C) and TaF_5 (m.p., 96.8 °C) are very hygroscopic and deliquesce in moist air. Both form clear solutions in water but corrode glass slowly. MF_6^- ions are formed with alkali fluorides (Ruff and Schiller; 1911). The structures of these fluorides were not known before 1945, although the isoelectronic ZrF_7^{3-} , NbF_7^{2-} and TaF_7^{2-} ions have a capped trigonal prism structure (Hoard; 1939).

Chromium Group elements — Deep green CrF_2 (m.p., 810 °C) is formed from chromium metal or chromium(II) chloride and hydrogen fluoride at red heat (Poulenc; 1893) and is isostructural with CuF_2 having a distorted rutile structure. Yellow-green crystals of CrF_3 form when CrCl_3 is heated with hydrogen fluoride at 550 °C (Poulenc; 1893, 1894). Both chromium fluorides are sparingly soluble in water. von Wartenberg (1941) obtained brown CrF_4 and light, volatile, fire-red CrF_5 as well as CrF_3 by fluorinating Cr, CrCl_3 or CrF_3 in an F_2 stream using a sintered alumina tube. CrO_2F_2 (b.p., 80 °C) was formed in the presence of O_2 . The vapour of CrF_4 is blue in colour. CrO_2F_2 also results from the reaction of the chloride with F_2 or hydrogen fluoride. In the fluorochromate KCrO_3F , formed by boiling chromates with hydrofluoric acid, the CrO_3F^- ion is tetrahedral [20].

Only one molybdenum fluoride, MoF_6 , had definitely been established by 1945 having been obtained from the elements. If the fluorine stream contains O_2 , some MoOF_4 and MoO_2F_2 are also formed. MoF_6 (m.p., 17.5 °C; b.p., 35.0 °C) is colourless and hygroscopic, and forms a colourless solution with water. The oxyfluorides MoOF_4 and MoO_2F_2 can also be obtained from the chlorides by reaction with hydrogen fluoride (Ruff and Eisner; 1907). Of interest is the complex $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$ in which the $\text{MoO}_3\text{F}_3^{3-}$ ion is octahedral [20].

Ruff repeated the experiments of Moissan, who had not been able to obtain a homogeneous product from the reaction of tungsten with fluorine. He successfully produced WF_6 from WCl_6 and hydrogen fluoride (Ruff and Eisner; 1905) or from SbF_3 or AsF_3 (Ruff, Eisner and Heller; 1907). WF_6

(m.p., 2.3 °C; b.p., 17.5 °C) is a colourless gas, being pale yellow in the liquid form. It decomposes in water to yield $\text{WO}_3(\text{aq.})$. The fact that WF_6 was more volatile than MoF_6 despite its greater molecular weight contradicted all the theories current at that time. This behaviour was only explained after 1945.

Manganese and rhenium fluorides — Pink crystals of MnF_2 may be obtained by reacting the carbonate with hydrogen fluoride (Moissan and Venturi; 1900). MnF_2 (m.p., 856 °C) crystallises with the rutile structure. It is slightly soluble in water but more so in hydrogen fluoride and acids. To obtain MnF_3 , it is necessary to react the iodide with fluorine (Moissan; 1900; von Wartenberg; 1940). The fluoride has a dissociation pressure < 0.1 atm at 600 °C (von Wartenberg; 1940). Wine-red MnF_3 is only slowly dissolved by water to yield MnF_2 , MnO_2 and hydrogen fluoride; it is, however, a strong fluorinating agent. When KMnO_4 is dissolved in hydrofluoric acid the salt K_2MnF_6 is obtained (Weinland and Lauenstein; 1899). The fluorite equipment available to Ruff enabled a successful study of the rhenium fluorides (Ruff and Kwasnik; 1932). At 125 °C rhenium and oxygen-free F_2 yield yellow ReF_6 [m.p., 18.8 °C; b.p., 47.6 °C (most recent value 33.7 °C)]. It is very hygroscopic and hydrolyses to give $\text{ReO}_3(\text{aq.})$. If the fluorine in these reactions contains O_2 , ReO_2F_2 (m.p., 156 °C) is produced in small quantities together with ReOF_4 (m.p., 39.7 °C; b.p., 62.7 °C) and ReF_6 . By reducing ReF_6 with H_2 , CO and SO_2 , the green ReF_4 (m.p., 124.5 °C) is obtained. K_2ReF_6 occurs as a green powder from the reaction of KReO_4 and HI in hydrogen fluoride (Ruff and Kwasnik; 1934).

Iron Group fluorides (Fe, Co, Ni) — Colourless iron(II) fluoride FeF_2 , like green iron(III) fluoride FeF_3 , is prepared by heating iron or the appropriate chloride with hydrogen fluoride at red heat (Poulenc; 1892, 1894). FeF_2 (m.p., > 1000 °C) crystallises with the rutile structure and is only poorly soluble in water. $\text{FeF}_2 \cdot 4\text{H}_2\text{O}$ is formed in the presence of moisture. FeF_3 (sublimes at > 1000 °C) has the AlF_3 structure (Ebert; 1931). Its low volatility contrasts with that of FeCl_3 . FeF_2 forms many complexes, e.g. M_3FeF_6 , where $\text{M} = \text{NH}_4, \text{Li}, \text{Na}, \text{K}, \text{Rb}$ or Cs . Its cubic structure resembles that of $(\text{NH}_4)_3\text{AlF}_6$ (Minder; 1937). Remy and Busch (1933) studied various $(\text{FeF}_5)^{2-}$ complexes, while the rapid formation of stable FeF_6^{3-} complexes is of value in analytical chemistry.

Pink cobalt(II) fluoride CoF_2 is obtained from CoCl_2 by heating in a hydrogen fluoride stream at 300 °C (Poulenc; 1892; Ruff and Ascher; 1929). CoF_2 (m.p., ca. 1200 °C) crystallises with the rutile structure and is only poorly soluble in water where it dissolves with hydrolysis. The fluoride forms the hydrates $\text{CoF}_2 \cdot 3\text{H}_2\text{O}$, $\text{CoF}_2 \cdot 4\text{H}_2\text{O}$ and complexes such as K_2CoF_4 and $\text{KCoF}_3 \cdot \text{H}_2\text{O}$. The bright brown cobalt(III) fluoride CoF_3 is obtained by heating CoCl_2 in a stream of fluorine at temperatures up to 300 °C. At 600 - 700 °C in an F_2 stream it volatilises, and must be stored in airtight quartz or metal bottles (Ruff and Ascher; 1929). It is doubtful whether the green CoF_3 which Barbieri and Calzolavi (1905) claimed to have produced ever existed. The structure of CoF_3 resembles that of FeF_3 . It does not

decompose into CoF_2 and F_2 at temperatures below 600°C as was stated in the literature up to 1950. At 600°C the dissociation pressure is <0.1 atm (von Wartenberg; 1940). CoF_3 turns dark brown in moist air; it reacts with water with the evolution of O_2 . It forms hydrates and complexes, e.g. $[\text{Co}(\text{NH}_3)_6]\text{F}_3$, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{F}_3$ or M_3CoF_6 (Blitz and Rahlfs; 1927), the cobalt(III) ion being stabilised in these complexes. It is often used in inorganic and organic chemistry as a fluorinating agent.

The sole nickel fluoride is green NiF_2 which is obtained by heating nickel powder in a hydrogen fluoride stream at 150°C (Poulenc; 1892; Ruff and Ascher; 1929; Henkel and Klemm; 1935). NiF_2 (sublimes at $>1000^\circ\text{C}$) crystallises in the rutile structure. It is not very soluble in water and basic products result. Complexes such as K_2NiF_4 and KNiF_3 have been synthesised. The latter compound crystallises in the perovskite type (Goldschmidt; 1927). References made in the literature to higher binary nickel fluorides have not been confirmed to date.

Platinum Group fluorides — The number of binary fluorides of the platinum metals produced prior to 1945 is small compared to those known today. Furthermore, the species described were not always definitely characterised. The yellow crystals described by Ruff and Tschirch (1913) as OsF_8 were, in fact, OsF_6 (Weinstock and Malm; 1956). Emerald-green RuF_5 , the only fluoride of this element known up to 1945, is obtained from the elements at 300°C . RuF_5 [m.p., 101°C (most recent value 86.5°C)] is decomposed by water, aqueous solutions of sodium hydroxide and hydrochloric acid (Ruff and Vidic; 1925). Red RhF_3 is obtained by heating the elements in a fluorite tube at red heat when a small amount of a bright brown volatile fluoride ($\text{RhF}_4?$) is also formed. RhF_3 is not isostructural with FeF_3 or CoF_3 as claimed by Ebert (1931), but with IrF_3 (Hepworth *et al.*; 1957). RhF_3 is very stable and resists water, acids and bases unless strongly heated (Ruff and Ascher; 1929; Ruff; 1928). Black PdF_3 is obtained from the elements at red heat, and PdF_2 which crystallises in the rutile structure (Ruff and Ascher; 1929) is formed as a by-product. PdF_3 is not isostructural with CoF_3 , and gives off O_2 with water and Cl_2 with hydrochloric acid. Structure analyses (undertaken after 1945) show that PdF_3 should be formulated as $\text{Pd}^{2+}\text{Pd}^{4+}\text{F}_6$. Complex fluorides of Ru, Rh and Pd were not known in their pure forms before 1945. Ruff and Tschirch (1913) and Ruff and Ascher (1929) investigated osmium fluorides. When heated in a fluorine stream, osmium metal yields OsF_8 (see above), yellow green OsF_6 (m.p., 34°C) and black OsF_4 , depending on the concentration of fluorine employed in the stream and the temperature. The OsF_4 produced by Hargreaves and Peacock (1960) has, however, entirely different properties from the OsF_4 produced by Ruff *et al.* Pale yellow IrF_6 (m.p., 44°C ; b.p., 53°C) which forms when iridium powder is heated in an F_2 stream at 260°C , is very hygroscopic and reacts with glass, presumably turning into IrOF_4 . An involatile, yellow brown oil is obtained by reacting IrF_6 with Ir metal. Originally identified as IrF_4 , it has now been conclusively shown to be IrF_5 (Bartlett and Rao; 1965). The only well-defined platinum fluoride known

up to 1945 was yellow brown PtF_4 which is produced from the elements by heating at 500°C (Moissan; 1891). PtF_2 was said to have been formed simultaneously, but has not been confirmed. PtF_4 has the same structure as RhF_4 , PdF_4 and IrF_4 . The structure of K_2PtF_6 , which Berzelius described and which was investigated by Ruff (1913) and Schlesinger and Tapley (1924), was not known up to 1945.

Uranium fluorides — Ruff and Heinzelmänn (1909) were the first to produce UF_6 by reacting F_2 with UCl_5 or uranium. The method employed was to admix some Cl_2 with F_2 at 250°C (formation of reactive chloro-fluorides). White UF_6 (sublimes at 56°C) is very hygroscopic, producing UO_2F_2 . UF_6 attacks glass and is thereby changed into UOF_4 and UO_2F_2 (von Grosse; 1932). Omission of chlorine results mainly in the formation of involatile green UF_4 . Its existence had not been definitely established in 1945. For technical reasons UF_6 was obtained from U_3O_8 and F_2 at 600°C (*FIAT Review* [7]).

Acknowledgement

I would like to thank Dr. Günther Beer for his help with the literature.

References

- 1 H. Moissan, *Ann. Chim. Phys.*, 25 (1892) 125.
- 2 H. Moissan, *Le Fluor et ses Composés*, Steinheil: Paris, 1900.
- 3 J. Burdon, B. Emson and A. J. Edwards, *J. Fluorine Chem.*, to be published.
- 4 M. A. Damiens, *Bull. Soc. Chim. Fr., Ser. 5,3* (1936) 1.
- 5 E. Einecke, *Angew. Chem.*, 50 (1937) 859.
- 6 H. J. Emeléus, *J. Chem. Soc.*, (1942) 441.
- 7 W. Klemm, *FIAT, Review of German Science 1939 - 1946*, Dieterich'sche Verlags, Wiesbaden, 1948.
- 8 *Gmelin's Handbuch der anorganischen Chemie*, 8. Auflage, System Nr. 5, Ergänzungsbände System Nr. 5, Verlag Chemie, Weinheim, Bergstrasse; Springer Verlag, Berlin, Heidelberg, New York.
- 9 W. Hückel, *Ber. Dtsch. Chem. Ges.*, 73 (1940) 125.
- 10 J. H. Simons (ed.), *Fluorine Chemistry*, Vol. 1, Academic, New York, 1950; H. J. Emeléus, "Non-volatile Inorganic Fluorides", p. 1; A. B. Burg, "Volatile Inorganic Fluorides", p. 77; H. S. Booth, "Boron Trifluoride", p. 189; J. H. Simons, "Hydrogen Fluoride", p. 225; C. H. Cady, "Preparation of Fluorine", p. 293; G. A. Cady, "Physical Properties of Fluorine", p. 315; G. Glockler, "The Theoretical Aspects of Fluorine Chemistry", p. 319.
- 11 W. Klemm, *Angew. Chem.*, 53 (1940) 25.
- 12 J. W. Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, London, 1960.
- 13 O. Ruff, *Angew. Chem.*, 20 (1907) 1217.
- 14 O. Ruff, *Die Chemie des Fluors*, Springer, Berlin, 1920.
- 15 O. Ruff, *Angew. Chem.*, 41 (1928) 737.
- 16 O. Ruff, *Angew. Chem.*, 46 (1933) 739.
- 17 O. Ruff, *Ber. Dtsch. Chem. Ges.*, 69 (1936) 181.
- 18 O. Ruff, *Chem.-Ztg.*, (1937) 6.
- 19 *Strukturbericht*, Vol. I - VII, Akad. Verlags-Ges. Leipzig, 1931.
- 20 A. F. Wells, *Structural Inorganic Chemistry*, 1st. Edn., Oxford University Press, Oxford, 1945.
- 21 D. M. Yost and J. B. Hatcher, *J. Chem. Educ.*, 10 (1933) 330.

BIOGRAPHIC NOTE

Oskar Glemser, born 12 November, 1911, received his Dr. Engineer degree in 1935 from the Technische Hochschule, Stuttgart. He graduated in organic chemistry but soon changed to inorganic chemistry, working with Robert Fricke on metal oxide/water systems. He joined the Institute for Inorganic Chemistry and Electrochemistry at the Technische Hochschule, Aachen in 1939, where he discovered new metal oxides and hydroxides of nickel, molybdenum and tungsten. Following his move to Göttingen in 1952, where he became Director of the Anorganisch-Chemisches Institut, he began research in the field of inorganic fluorides, *i.e.* sulphur-nitrogen-fluorine compounds and



O. Glemser

various non-metal and metal fluorides. He has also studied gaseous hydroxides, the isopolyanions of vanadium, molybdenum and tungsten, and developed a new synthesis for carbon tetrachloride. In 1934 he was awarded the William Küster Prize from the Technische Hochschule, Stuttgart. In 1970 he received the Liebig Denkmünze from Gesellschaft Deutscher Chemiker, in 1972 the silver medal from the University of Helsinki, and in 1981 the Jozef Stefan medal from the Jozef Stefan Institute in Ljubljana, Jugoslavia. He is an honorary doctor of the University of Stuttgart (1976), Besançon, France (1978) and Braunschweig (1982). He was President of the Academy of Science in Göttingen (1962 - 70), President of the Gesellschaft Deutscher Chemiker (1976 - 7) and President of the Inorganic Division of IUPAC (1969 - 73).

Oskar Glemser is a member of the Akademie der Wissenschaften in Göttingen, the Österreichische Akademie der Wissenschaften in Vienna, the Deutsche Akademie der Natur Forscher 'Leopoldina' in Halle, the Centro di Logica e Scienze Comparate in Bologna, the New York Academy of Science, the American Association for the Advancement of Science and an associate member of Jozef Stefan Institute in Ljubljana.