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Reaction of Fluorine and Non-metal Fluorides in an Electric Discharge

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Fluorine reacts readily with the majority of substances at room or moderately elevated temperatures. Only in a few cases is special activation of the reactants necessary. An electric discharge may be used for this purpose. This review deals with studies of reactions involving elemental fluorine and fluorides in a gas discharge. Reactions which may be of preparative value are mainly considered.
The bibliography includes 113 references.

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I. INTRODUCTION

The use of electrical discharges in gases for preparative purposes in inorganic chemistry is generally known. The activating effect of the discharge makes possible reactions which cannot be achieved by thermal activation of the starting material or in the absence of a discharge by high temperatures and pressures alone.

Fluorine readily interacts with the majority of substances at room or moderately elevated temperatures. An exception are the reactions of fluorine with its nearest neighbours in the Periodic System: nitrogen, oxygen, and noble gases. In those cases where thermal activation of the starting materials does not lead to reaction or the expected products are unstable at high temperatures and therefore cannot be isolated, factors acting upon the reactant, such as an electric discharge or irradiation, become particularly important.

At low pressures and currents the plasma of a glow discharge is characterised by a low molecular temperature, amounting usually to several hundred degrees Kelvin, and a considerably higher electronic temperature. When the reaction is carried out in a discharge, the walls of the reactor may be cooled to very low temperature. Thus in syntheses in a discharge two conditions necessary for the formation of thermally unstable compounds are immediately fulfilled; in a low-temperature discharge plasma high concentrations of active species are established and the possibility of rapid quenching prevents the decomposition of the compounds formed.

The present review deals with studies on the reactions of fluorine with nitrogen, oxygen, krypton, xenon, and chlorine in an electric discharge. At normal temperatures and pressures molecular fluorine does not react with the above elements. In a discharge fluorine becomes more active due to its dissociation into atoms. The excited $^1\Pi_u$ state of the F_2 molecule has a repulsive potential curve[1]. The transition $^1\Sigma_g^+ \rightarrow {}^1\Pi_u$ leads to the dissociation of F_2 into two non-excited fluorine atoms (in the $^3P_{3/2}$ state). One cannot exclude the possibility that

ionised atoms and fluorine molecules present in the discharge participate in the reaction. For example, the emission spectrum of fluorine excited by an electric discharge[2] shows emission bands which were assigned to the F_2^+ ion.

The inclusion in the review of a section dealing with the reactions of nitrogen fluorides was dictated by the considerable interest which the reactions of this group of fluorides have attracted in recent years.

II. INTERACTION OF FLUORINE WITH NITROGEN

Many reactions leading to the formation of both binary† nitrogen fluorides and those containing other elements have been investigated. A characteristic feature of these reactions is the synthesis of nitrogen fluorides from nitrogen-containing compounds[3-5]. This review deals with the reactions of fluorine with elemental nitrogen.

The synthesis of nitrogen fluorides from the elements is thermodynamically possible. A mixture of fluorine and nitrogen constitutes a system in a state of metastable equilibrium which must overcome a high activation barrier for reaction to occur. If the reaction between fluorine and nitrogen occurs then, in accordance with the large negative free energy of nitrogen trifluoride ($\Delta G^\circ_{298} = -21.38$ kcal mole^{-1}) [6], a stoichiometric mixture of fluorine and nitrogen will be fully converted at room temperature into nitrogen trifluoride. The equilibrium constants[6] for the reaction $\frac{1}{2}N_2 + \frac{3}{2}F_2 \rightleftharpoons NF_3$ at a pressure of 1 atm at 298°K is of the order of 10^{14}. The absence of an appreciable reaction between fluorine and nitrogen is evidently due to kinetic factors.

Attempts were made as early as the beginning of the century to obtain nitrogen fluoride in a discharge[7]. A study was made of the effect of an arc on a mixture of gaseous fluorine and nitrogen and also of a spark discharge on a liquid mixture of the same substances. However, the formation of nitrogen fluoride in these experiments could not be established[7].

The synthesis of nitrogen trifluoride in a glow discharge with a yield of about 30% was reported in 1964 [8]. Mixtures of fluorine and nitrogen were passed through the discharge at a pressure of 20–40 mmHg, the walls of the tube being cooled with liquid nitrogen. Variation of the ratio $F_2 : N_2$ in the initial mixture did not lead to the synthesis of nitrogen fluorides other than NF_3. The compound was obtained also in a discharge at a current of 10–15 mA and a pressure of 10–17 mmHg, the reactor being maintained at temperatures ranging from −150 to −196°C.[9]

The synthesis of nitrogen fluoride in a discharge-flow apparatus at a pressure of 15 mmHg has been described[10]. The volume flow rate of the fluorine–nitrogen mixtures was varied from 0.09 to 1.20 litre h^{-1} (the volumes of the gases at s.t.p. are indicated). The nitrogen trifluoride formed in the discharge condensed on the walls of the discharge tube immersed in liquid nitrogen. The conversion of the fluorine–nitrogen mixture rises to 60–70% as the volume flow rate is reduced to about 0.1 litre h^{-1} at a current of 10 or 25 mA. The conversion is almost independent of the composition of the initial fluorine–nitrogen mixtures.

The authors of the review[11] carried out experiments with a stoichiometric mixture ($F_2 : N_2 = 3 : 1$). The gases were passed through a discharge tube and the NF_3 formed was condensed in a trap at −196°C at a distance of 12 cm from the discharge zone. After the removal of the cold trap from the discharge, the yield of NF_3 fell. An increase of the current from 4 to 12 mA entails an increase of conversion, which, however, falls as the current is raised further to 25 or 40 mA. This phenomenon may be explained by an increase in the importance of the reverse reaction with increasing power of the discharge[11].

Since a high conversion of fluorine–nitrogen mixtures in a glow discharge is attained at low flow rates, the absolute yield of NF_3 per unit time is low. The synthesis of nitrogen trifluoride in a discharge is scarcely practicable for the preparation of the substance in large amounts. Usually the compound is obtained by the electrolysis of an ammonium hydrogen fluoride melt. Nitrogen fluoride was in fact, first synthesised in this way[12]. The electric discharge method has a certain advantage in that the compound obtained in a glow discharge is free from impurities, which are present in the substance synthesised electrolytically.

Nitrogen trifluoride is formed in very low yields (1.5–2%) in a silent (electrodeless) discharge when a mixture of fluorine and nitrogen is circulated through an ozoniser[13].

$\Delta G^\circ_{298} = 18.72$ kcal mole^{-1} for the formation of tetrafluorohydrazine from the elements, ΔG°_T becoming negative only at temperatures below −243°C [6]. However, when the experiments in a gas discharge are carried out under conditions of rapid flow, it is possible to obtain a low yield of tetrafluorohydrazine from the elements. The NF_2 radicals formed as an intermediate in the reaction between fluorine and nitrogen are stabilised to N_2F_4 as a result of the rapid cooling of the reaction mixture on quenching. Thus a stream of nitrogen was passed[14] through an arc discharge (300 A, 40 V) at a rate of 15 litre min^{-1} and mixed with gaseous fluorine. The reaction products entered a trap cooled with liquid nitrogen. The yield of nitrogen trifluoride and tetrafluorohydrazine did not exceed 1%.

About 1% of bound nitrogen was obtained on mixing carbon tetrafluoride with nitrogen plasma[15]. The quenching products contained nitrogen trifluoride, tetrafluorohydrazine, and traces of difluorodiazines. The reaction of sulphur hexafluoride with a nitrogen plasma also gives about 1% of bound nitrogen, largely in the form of the trifluoride[15]. The synthesis of nitrogen trifluoride under the action of an arc rotated by a magnetic field in a mixture of carbon tetrafluoride and nitrogen has been described[16]. The syntheses of nitrogen fluorides in plasma devices are considered in detail in the book edited by Baddour and Timmins[17].

The energy losses per unit volume of the reacting gases in the synthesis of NF_3 in a discharge are very large. Thus a conversion of 54% was achieved[11] at a specific energy[18] of 325 W h litre^{-1}. The high energy losses are evidently due to the need to activate the nitrogen molecules. The published data are as yet insufficient to decide which active forms of nitrogen participate in the synthesis of nitrogen trifluoride. The intermediates in the reaction of fluorine with nitrogen may be the radicals NF and NF_2. NF radicals have been detected both in the emission spectrum of nitrogen fluoride which has passed through a microwave discharge[19,20] and in the emission spectrum of the flame formed when hydrogen burns in nitrogen trifluoride[21]. However, it is difficult to state definitely as a result of which process NF radicals might have been generated in the synthesis of NF_3 in a discharge.

† Binary nitrogen fluorides are defined as those which consist only of fluorine and nitrogen: NF_3, N_2F_4, N_2F_2, FN_3.

To determine the mechanism of the synthesis of nitrogen trifluoride from the elements, spectroscopic studies on the interaction between fluorine and nitrogen in a discharge would be useful. The reaction of active nitrogen and molecular fluorine has not apparently been investigated[22].

In an electric discharge it is possible to obtain substances in greater yields than those corresponding to thermodynamic equilibrium[18]. For example, nitric oxide synthesised from the elements is formed in amounts greatly exceeding the thermodynamic equilibrium value[18,23]. As already mentioned, at low temperatures the equilibrium $\frac{1}{2}N_2 + \frac{3}{2}F_2 \rightleftharpoons NF_3$ is fully displaced to the right. Electric discharge in a mixture of fluorine and nitrogen displaces the system from a state of metastable equilibrium and brings it closer to thermodynamic equilibrium, i.e., the effect of the discharge is in this case comparable to that of a catalyst.

III. REACTIONS OF NITROGEN FLUORIDES IN A DISCHARGE

Nitrogen trifluoride is decomposed into its elements in a glow discharge. At low flow rates a steady-state degree of decomposition is attained, amounting to about 80% at a current of 15 or 25 mA. [10] The dissociation of NF_3 may be represented by the following sequence of reactions:

$$NF_3 \rightleftarrows F + NF_2 \rightleftarrows 2F + NF \rightleftarrows {}^3/_2F_2 + {}^1/_2N_2.$$

Tetrafluorohydrazine was not detected in the NF_3 decomposition products[10]. The NF_2 radicals, which are suggested by this decomposition mechanism, either undergo further defluorination or combine with a fluorine atom regenerating the nitrogen trifluoride. When the fluorine formed in the decomposition of NF_3 is removed, for example by reaction with mercury vapour, it is possible to obtain tetrafluorohydrazine and difluorodiazines from nitrogen trifluoride[24]. According to the literature[24], the yields of N_2F_4 and N_2F_2 relative to the unreacted nitrogen trifluoride were respectively 51–67 and 12–16%. The discharge tube was maintained at a temperature of about 200°C. At a higher temperature (320–330°C) the reaction

$$2NF_3 + 2Hg = N_2F_4 + Hg_2F_2$$

also takes place without an electric discharge.[25]

The synthesis of tetrafluorohydrazine in the decomposition of nitrogen trifluoride in a discharge may be compared with the synthesis of hydrazine from ammonia in a discharge[26–29]. One of the reasons for the low yield of hydrazine in its synthesis from ammonia is the breakdown of the N_2H_4 formed by hydrogen atoms. Acceleration of the recombination of atomic hydrogen leads to an increased yield of hydrazine. Tetrafluorohydrazine is obtained from nitrogen trifluoride in a discharge provided that the fluorine formed reacts with mercury, which is a fluorine acceptor.

The synthesis of hydrazine from ammonia and of tetrafluorohydrazine from nitrogen trifluoride is described by the following general equation:

$$2AX_3 = A_2X_4 + X_2.$$

Other reactions described by the same general equation occur in an electric discharge: the synthesis of P_2Cl_4 from phosphorus trichloride[30] and of B_2Cl_4 from boron trichloride[31,32]. However, B_2F_4 has not been obtained in a discharge from boron trifluoride[33].

Tetrafluorohydrazine is obtained by heating nitrogen trifluoride in the presence of fluorine acceptors, for example metals[34]. The possibility of synthesising N_2F_4 from NF_3 arises because of the relative stability of NF_2 radicals and the absence of high concentrations of fluorine atoms. On the other hand, in a glow discharge tetrafluorohydrazine is unstable in relation to its decomposition products – nitrogen trifluoride and nitrogen. Tetrafluorohydrazine readily decomposes, with a small expenditure of energy, forming nitrogen trifluoride[11]:

$$N_2F_4 = {}^4/_3NF_3 + {}^1/_3N_2.$$

With increase in the energy density, more far-reaching breakdown takes place:

$$N_2F_4 \rightarrow NF_3;\ NF_3 \rightleftarrows {}^1/_2N_2 + {}^3/_2F_2.$$

The low stability of tetrafluorohydrazine in a glow discharge prevents the occurrence of difluoroamination reactions in a discharge using N_2F_4.

The first reports on the synthesis of the compound F_3NO appeared in 1966.[35–38] The compound is called nitrogen oxytrifluoride or trifluoroamine oxide. The latter name emphasises the formal similarity of F_3NO to the amine oxides $R_3N \rightarrow O$ and is used more often. The possibility of synthesising F_3NO provides evidence as to the valency, coordination unsaturation of the nitrogen atom in nitrogen trifluoride.

Trifluoroamine oxide is formed when a discharge acts upon the following mixtures: fluorine–air[39], fluorine–nitrogen oxides[39], and nitrogen trifluoride–oxygen difluoride[40,41]. The synthesis of F_3NO by the action of a discharge on an equimolar mixture of nitrogen trifluoride and oxygen has been reported and the method has been described in greater detail in a later paper[42]. The mixture of starting materials is passed at a rate of 1.7–3.4 litre h^{-1} through a discharge tube in liquid nitrogen. A pressure of 10–15 mmHg and a current of 30–50 mA are maintained in the apparatus. Under these conditions, about 70% NF_3 reacts, the yield of F_3NO amounting to 10–15%. The reaction products are also nitrogen oxides and dioxygen difluoride. When the discharge tube is thermostatted at −78°C, trifluoroamine oxide is not formed.

The mechanism of the synthesis of F_3NO from nitrogen trifluoride and oxygen in a discharge is obscure. Since nitrogen trifluoride readily dissociates, one cannot exclude the possibility that trifluoroamine oxide is in fact one of the decomposition products of nitrogen trifluoride, formed, for example, in the following way:

$$NF_3 = {}^1/_2N_2 + {}^3/_2F_2;\ {}^1/_2N_2 + {}^1/_2O_2 = NO \qquad NO + F = NOF;\ NOF + 2F = F_3NO.$$

In this case nitrogen trifluoride serves simply as a source of fluorine and nitrogen. One can also imagine a direct synthesis of F_3NO—by the reaction of activated (atomic) oxygen with nitrogen trifluoride activated in a discharge:

$$NF_3 + O = F_3NO.$$

Molecular oxygen and certain other oxidants do not interact with nitrogen trifluoride in the absence of a discharge[42–44]. Other reactions[35–37,45–52] leading to the formation of trifluoroamine oxide do not involve the use of an electric discharge. Although it is at present difficult to state a preference for any one of the methods described for the synthesis of F_3NO, the synthesis in a discharge from nitrogen trifluoride and oxygen appears to be fairly simple and the starting materials are available.

The formation of the cation NF_4^+ also indicates the coordination unsaturation of nitrogen in the NF_3 molecule. In 1966 reports were published[52,53,54] on the preparation of two salts with this hitherto unknown cation: hexafluoroarsenate ($NF_4^+AsF_6^-$) and hexafluoroantimonate ($NF_4^+SbF_6^-$). The first compound has been obtained both in a discharge[53,55] and by heating the same starting materials under pressure[56]. In the electric-discharge synthesis of $NF_4^+AsF_6^-$ a mixture of NF_3, AsF_5, and F_2 in molar proportions of 1 : 1 : 2 was passed into a glass reactor cooled to −78°C. The initial pressure of the gaseous mixture in the reactor was about 80 mmHg. After 35–42 h, about 1 g of $NF_4^+AsF_6^-$ was obtained in the circulation system. The formation of this salt may be represented by the equation

$$NF_3 + F_2 + AsF_5 = NF_4^+AsF_6^-,$$

which postulates a heterolytic dissociation of the fluorine molecule.

IV. SYNTHESIS OF OXYGEN FLUORIDES

Oxygen fluorides with the general formula O_nF_2 (n = 2–6) are extremely reactive. They react with many substances at temperatures as low as −196°C. Polyoxygen difluorides are obtained from fluorine and oxygen in a glow discharge. Since the compounds are stable only at very low temperatures, the discharge reactor must be cooled during the synthesis.

In the preparation of dioxydifluoride O_2F_2, a mixture of gases with a ratio $F_2 : O_2 = 1 : 1$ by volume or containing a small excess of fluorine is admitted into a discharge tube cooled with liquid air or liquid nitrogen[57–60]. A current of several tens of milliamperes is maintained in the discharge. The O_2F_2 produced is condensed on the walls of the discharge tube in the form of a solid, the vapour pressure of which is 0.01 mmHg at −168°C [44]. The yield of O_2F_2 falls with increasing flow rate of the fluorine–oxygen mixture but more than half of the mixture passed through the discharge is converted into dioxygen difluoride even at specific energies of 5–7 W h litre^{-1} [11]. The synthesis of dioxygendifluoride in a glow discharge may be accompanied by the formation of ozone[44,58]. It has been shown[61] that ozone is formed in an appreciable amount only at high specific energies.

Dioxygendifluoride is not formed solely by the reaction of fluorine with oxygen in a glow discharge. The photochemical reaction of fluorine with ozone on irradiation with light of wavelength 3650 Å at −153°C yields dioxygendifluoride and oxygen difluoride[62]. On the other hand, when a mixture of fluorine and ozone is irradiated at a higher temperature (0° and 20°C), ozone decomposes with formation of oxygen[63]:

$$F_2 + O_3 + h\nu\,(3650\text{Å}) \rightarrow F_2 + {}^3/_2O_2.$$

Trace amounts of O_2F_2 are formed when a mixture of F_2 and O_2 is irradiated with light from a mercury lamp at a temperature of −42°C [64].

The compound with the formula O_3F_2 was apparently obtained for the first time in 1938. [65] The synthesis of O_3F_2 in a glow discharge was described in 1959. [66] The conditions for the preparation of trioxygen difluoride ("ozone fluoride") did not essentially differ in any way from the conditions for the synthesis of O_2F_2 with the exception that the initial mixture of gases for the synthesis of O_3F_2 contained three volumes of oxygen and two volumes of fluorine. Trioxygendifluoride frozen at −196°C was converted into O_2F_2 under the action of fluorine activated in the discharge. Trioxygendifluoride did not react with molecular fluorine at −196°. [66]

In 1961 the synthesis of the oxygen fluoride O_4F_2 was described[67]. To prepare this compound, a mixture of two volumes of oxygen and one volume of fluorine was introduced into a discharge tube cooled to −196°C. Tetraoxygendifluoride is a reddish-brown substance melting at −191° ± 2°C and a vapour pressure of 0.25 mmHg at −183°C. [68] On increase in temperature to −163°C, O_4F_2 decomposes into oxygen and dioxygendifluoride; rapid heating results in the explosion of tetraoxygendifluoride. An improved method for the synthesis of O_4F_2 has been described[68]. In a discharge tube, made partly of copper to improve the removal of heat, a yield of 180 mg of O_4F_2 per hour was achieved. The discharge tube was maintained at temperatures between −203 and −213°C.

The oxygen fluorides O_5F_2 and O_6F_2 were obtained from fluorine–oxygen mixtures with the reactant ratios $O_2 : F_2$ = 5 : 2 (for O_5F_2) and 3 : 1 (for O_6F_2). The discharge tube was cooled to −213°C and the power of the discharge was varied in the range 1.6–6 W. [69] Apart from fluorine–oxygen mixtures, a mixture of oxygen difluoride and oxygen was employed for the synthesis of O_2F_2, O_3F_2, and O_4F_2 in a discharge[70].

Thus the results published up till 1967 show that fluorine and oxygen react in an electric discharge with formation of oxygen fluorides O_nF_2 (n = 2–6). The preparation of a particular compound is determined by the composition of the initial fluorine–oxygen mixture and the conditions of the synthesis. Higher members of the family of polyoxygendifluorides are formed at a low current and a low discharge power, a low reactor wall temperature, and a low flow rate of the starting materials into the discharge. Subsequent investigations altered somewhat the postulates established by 1967.

The existence of the compound with the formula O_3F_2 and the possibility of its synthesis in a glow discharge were questioned. Nebgen et al.[71] concluded that trioxygendifluoride is dioxygendifluoride with "intermediate" oxygen, which is retained in dioxygendifluoride too tenaciously to be regarded as dissolved but at the same time too weakly to postulate the formation of a chemical bond. Malone and McGee[72] regarded O_3F_2 as a mixture of weakly bound radicals FO and O_2F. In his review Turner[73] expressed well founded doubts concerning the existence of trioxygendifluoride and substances with the empirical formulae O_5F_2 and O_6F_2.

It has been shown[74] that the so-called trioxygendifluoride is a mixture of O_2F_2 and O_4F_2 in equilibrium with the radicals O_2F, which decompose on raising the temperature:

$$\begin{matrix}[O_2F_2, & O_4F_2] \\ & \downarrow\downarrow \\ & 2OOF \rightarrow O_2F_2 + O_2.\end{matrix}$$

An additional study[75] on the existence of the species O_3F_2 by ^{19}F and ^{17}O NMR spectroscopy and also the study of the formation of dioxygenyl tetrafluoroborate from boron trifluoride and trioxygendifluoride confirmed these conclusions of Solomon et al.[74] It was shown[75] that the models[71,72] proposed for O_3F_2 are incorrect.

Another important result obtained recently is a development of a method for the synthesis of dioxygendifluoride not involving an electric discharge. The preparation of O_2F_2 by the radiolysis of a mixture of liquid fluorine and oxygen at −196°C was reported[76]. The synthesis was described in detail in a later communication[77]. The starting materials were subjected to the action of 3 Mev bremsstrahlung. Goetschel et al.[77] were probably the

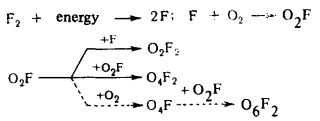
first to obtain pure dioxygendifluoride. The pure compound in the solid state is coloured yellow and not orange as usually stated in earlier communications. The melting point of O_2F_2 (–154.1°C) [76,77] differs appreciably from the value found previously (–163.5°C) [56]. Dioxygendifluoride without an admixture of O_2F radicals is diamagnetic. Data have been presented[77] indicating the possible existence of the radical O_4F.

The synthesis of dioxygendifluoride in a glow discharge in large amounts does not require any special equipment apart from a single-phase high-voltage transformer. The synthesis in an electric discharge has the advantage of simplicity over the radiolysis of liquid fluorine and oxygen.

The synthesis of oxygen fluorides in an electric discharge involves the intermediate formation of the O_2F radical. The existence of the O_2F radical (dioxygenmonofluoride) has now been reliably established[78–87]. The radical is relatively long-lived at –180°C [82], its average lifetime at temperatures between –180 and –160°C has been estimated[85] as 20 min. The study where it was shown that the O_2F radical exists in the gas phase at room temperature is of great interest[88]:

$$O_2BF_4(\text{solid}) \rightleftharpoons O_2F(\text{gas}) + BF_3(\text{gas}).$$

The available data[61,75,77–79] can be rationalised in general terms by the following mechanism for the synthesis of oxygen fluorides:



The energy necessary for the dissociation of fluorine is imparted to the F_2 molecule by photolysis, radiolysis, or in a discharge. The reaction pathway indicated by a dashed line is regarded as probable.

The synthesis in a discharge of OF_2, which is thermally stable up to 200–250°C, has not been described. The action of a glow discharge on fluorine–oxygen mixtures at a low pressure with the reactor cooled in liquid nitrogen does not apparently lead to success. The synthesis of O_2F_2, which has the advantage that its occurrence does not require the dissociation of molecular oxygen, competes with the synthesis of OF_2, which does require such dissociation.

V. SYNTHESIS OF NOBLE GAS FLUORIDES

In 1962 the existence of noble gas compounds was discovered[89]. Certain noble gas fluorides were obtained in an electric discharge soon after this discovery. In the synthesis of xenon fluorides the walls of the discharge reactor or an insert introduced into the reactor are cooled to –78°C. The compounds obtained are synthesised on the cold surface in the reaction zone.

In the synthesis of XeF_2 using a discharge produced by an induction coil, mixtures of gases with $Xe:F_2$ ratios ranging from 1:1 to 1:3 were employed. The yield of the product reached 0.1 g h^{-1}. [90,91] XeF_2 is obtained in higher yields from a mixture with $Xe:F_2 = 1:1$ (by volume) in a glow discharge[92]. For a mixture flow rate of about 1 litre h^{-1} and a current of 30–90 mA, 3.4–3.7 g of xenon difluoride may be obtained after 1 h in the discharge[92]. Xenon difluoride has been obtained[93] by passing mixtures containing approximately equal volumes of Xe and CF_4 through a glow discharge. In this case the yield of XeF_2 was 0.05–0.15 g h^{-1} for a gas flow rate of 1–2 litre h^{-1}.

In the synthesis of xenon tetrafluoride a mixture with $Xe:F_2 = 1:2$ (by volume) was introduced into the discharge at a rate of about 0.14 litre h^{-1}. [94] The yield of XeF_4 reached 1.5 g after 3.5 h in the discharge at a current of 12–31 mA. Xenon hexafluoride has been synthesised from a mixture with $Xe:F_2 = 1:3$ (by volume)[94]. The mixture was passed into the discharge at a rate of 0.016 litre h^{-1}. [95] The possibility of synthesising xenon oxide fluorides by reacting xenon with oxygen difluoride in a discharge has been reported[44,95].

Apparently in the synthesis of xenon fluorides in a discharge the composition of the product is determined to some extent by that of the initial mixture of reactants, since in the synthesis of XeF_2, XeF_4, and XeF_6, mixtures with $Xe:F_2 = 1:1$, 1:2, and 1:3 respectively were employed. Probably the xenon difluoride formed initially is fluorinated to XeF_4 or XeF_6 if the fluorine content in the initial mixture exceeds 50 vol.% and the gases are passed into the discharge at a sufficiently low rate.

In the synthesis of xenon fluoride the dissociation of fluorine is a process requiring activation. The excitation of xenon atoms in the discharge[96] is not an essential condition for the synthesis of the fluorides.

Xenon difluoride may be synthesised photochemically by irradiating mixtures of xenon and fluorine or oxygen difluoride with sunlight or ultraviolet light[97–101]. Gaseous fluorine begins to absorb in the visible region, and this absorption reaches a maximum in the near ultraviolet at 2845 ± 5 Å. [102] The excitation of noble gas atoms requires a very high expenditure of energy. For example, the energies required to excite xenon atoms to metastable and resonance states are respectively 8.32 and 8.45 eV, [103] i.e. in order to excite 1 g-atom of xenon into either of these states more than 190 kcal would be required. Radiation with an energy of about 190 kcal per einstein has a wavelength of about 1500 Å, corresponding to the Schumann ultraviolet region, which is difficult to attain experimentally. The synthesis of XeF_2 by irradiating with daylight mixtures of fluorine and xenon in Pyrex reaction vessels[98,99,101] confirms the possibility of the reaction of fluorine atoms with unexcited xenon atoms. The fluorination of xenon at low temperatures with the aid of O_2F_2 [104,105] or O_4F_2 [68] in all probability also constitutes a reaction of atomic fluorine, formed as a result of the breakdown of oxygen fluorides, with unexcited xenon atoms.

When a high-frequency (25 MHz) discharge acts on mixtures of xenon, fluorine, and silicon or carbon tetrachloride, xenon difluoride, identified by mass spectrometry, is formed[106]. According to Meinert[106], the XeF_2 formed initially exchanges halogen atoms with $SiCl_4$ or CCl_4. When a mixture of xenon with chlorine and fluorine is exposed to a high-frequency (25 MHz) discharge or ultraviolet light, chlorine tri- and penta-fluorides are formed and not xenon halides[107].

In the fluorination of krypton the discharge reactor must be cooled to –183° or –196°C. Krypton fluoride was obtained in a discharge at a current of 24–37 mA and a pressure of 7–12 mmHg [95,108]. A mixture with $Kr:F_2 = 1:2$ (by volume) was employed for the synthesis and it was thought[95,108] that the product was krypton tetrafluoride. It soon became known[109] that, under conditions corresponding to those described above[108], krypton difluoride and not tetrafluoride is obtained. Krypton difluoride was synthesised in a circulation apparatus with a Pyrex discharge tube[109]. A mixture of fluorine and krypton with $Kr:F_2 = 1:2$ or 1:1.1 was admitted into the apparatus, the current being 15–20 mA. The yield of

KrF_2 reached 75% relative to the krypton taken for the synthesis, 0.25 g of KrF_2 being obtained after 1 h. To avoid the contamination of krypton tetrafluoride by silicon tetrafluoride, it has been suggested that KrF_2 be synthesised in a metallic discharge reactor[110].

The synthesis of krypton difluoride in a glow discharge is the only convenient method for the preparation of this compound. The photochemical reaction of krypton and fluorine[111] is very slow: after 1 day 2–3 mg of KrF_2 is formed from a mixture of the gases in a 2 litre vessel at atmospheric pressure.

VI. SYNTHESIS OF CHLORINE PENTAFLUORIDE.

The halogen derivatives of fluorine are obtained from the appropriate elements in the cold or with moderate heating. During the search for methods of synthesising higher chlorine fluorides, the possibility of preparing chlorine pentafluoride in a discharge was investigated. Chlorine pentafluoride is formed when a mixture of chlorine and fluorine or certain chlorine- or fluorine-containing compounds are exposed to an electric discharge (an a.c. or d.c. discharge or a discharge produced by a radiofrequency oscillator)[112]. In the synthesis of ClF_5 from fluorine and chlorine, mixtures were employed in which the fluorine content exceeded the stoichiometric proportion. An example of the synthesis of ClF_5 in a glow discharge where the initial mixture contained 10 volumes of fluorine for one volume of chlorine has been described[112,113]. The mixture of gases was passed at a rate of 1.5 litre h^{-1} through a discharge tube cooled to −78°C. A pressure of 30 mmHg was maintained in the apparatus. The reaction products—chlorine mono-, tri-, and penta-fluoride—were condensed in a trap at −196°C. The yield of ClF_5 was approximately 1 cm^3 (probably 1 cm^3 of gaseous ClF_5 is meant) in 4 litres of the initial mixture of gases[113]. The synthesis of ClF_5 in a discharge is interesting only as yet another example of reactions with participation of fluorine.

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The literature available on gas-discharge reactions deals mainly with traditional problems in gas electrochemistry, such as the synthesis of ozone, oxidation of nitrogen, and the cracking of hydrocarbons. The number of studies dealing with the reactions of halogens and halogen-containing compounds in a discharge has increased considerably in the last decade, but these reactions nevertheless still remain relatively little investigated.

Little attention has been devoted to the kinetics of the reactions of fluorine and fluorides in a discharge. The description in certain papers of "typical" experiments frequently illustrates only the reaction occurring in the discharge, providing information about the results of an individual experiment but not about the course of the reaction under conditions other than "typical". Non-metal fluorides are obtained mainly in a.c. glow discharges at mains frequency. The preparative scope of discharges of other types is virtually unknown.

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