THE PREPARATION OF DISULPHUR DECAFLUORIDE

by

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The amounts of S_2F_{10} obtained by direct fluorination of sulphur are determined by the rate of fluorine flow, the amounts of solid and gaseous diluent, and the temperature of the reaction tube.

Yields of S_2F_{10} from 5 to 10 per cent on sulphur reacted have been obtained by fluorination of a sulphur smoke.

Moisture and oxygen have been found to inhibit the formation of S_2F_{10} and SF_6.

A mechanism for the formation of S_2F_{10} which involves the progressive fluorination of an S - S linkage has been postulated.

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GENERAL INTRODUCTION

In 1940 attempts were made at McGill University to produce samples of pure sulphur hexafluoride as part of a search for possible toxic respirator penetrants (1). Surprisingly, the samples of supposedly pure hexafluoride, formed by passing fluorine over sulphur, were found to be toxic in small concentrations. Purification and fractionation of the sample resulted in the isolation of a high molecular weight component identical in properties with the compound disulphur decafluoride (S_2F_{10}) discovered and described by Denbigh and Whytlaw-Gray in 1934 (2,3). It was then shown that the poisonous effects exhibited by the sulphur hexafluoride were due to the relatively small concentrations of S_2F_{10} present as impurity. Toxicity studies soon indicated that the remarkable physiological properties of S_2F_{10} made it very valuable as a potential chemical warfare agent (4).

Since that time extensive research has been carried out in Canada, United States, and Great Britain on the production and properties of S_2F_{10}. Because all methods of obtaining the gas would involve the use of the relatively costly raw material, fluorine, investigations everywhere were concerned with attempts to find suitable methods of producing yields of S_2F_{10} large enough to make commercial production feasible.

The work done at McGill has at all times emphasized

the practical nature of the problem. The mechanism of formation of S_2F_{10} was studied only insofar as it had immediate bearing on the achievement of higher yields.

It has been shown that practicable yields are possible only when solid sulphur is allowed to react with gaseous fluorine under controlled conditions. When this is done, varying amounts of sulphur fluorides and oxyfluorides are produced as by-products. Of these, SF_6 and SO_2F_2, as well as S_2F_{10}, are unaffected by dilute caustic solutions, whereas a second group of compounds, herein referred to as lower fluorides (L.F.), are totally decomposed or absorbed. The possible fluorides in the latter group are S_2F_2, SF_2, SF_4, SOF_2, SOF_4, and a little SO_2F_2.

This thesis embodies the investigation of the solid sulphur-gaseous fluorine reaction, and the effect of several variables on this system. An attempt has been made to postulate a mechanism for the reaction although the data obtained are much more useful from a production viewpoint.

HISTORICAL

Generation of Fluorine

Nearly all methods that have been used for the production of fluorine involve the electrolysis of the system hydrogen fluoride - potassium fluoride at different temperatures in different cell designs. Cady has measured the freezing points and vapor pressures of this system and has shown that there are three different temperature ranges in which fluorine can be prepared conveniently, -80° to -20°C, 70° to 110°C and 220° to 300°C (5). In all these regions the system is liquid and the vapor pressure of hydrogen fluoride is at a minimum and less than 25mm. Although most cells have been designed to operate at these points, other temperatures have been employed in later years.

Moissan first prepared fluorine at low temperatures by the electrolysis of a solution of pure HF rendered conducting with a little dissolved KF (6). The electrodes used were platinum and the electrolyte was kept at approximately -20°C. Since this requires HF, which is extremely corrosive, reacting with and destroying most metals, many difficulties arise in the operation of cells at this temperature.

Schumb, Gamble, Anderson and Stevens have described a fluorine generator that operates at 20° to 40°C and uses nickel anodes, steel containers and electrolyte of composition KF (8 - 9) HF (7). Because of the high vapor

pressure of HF at this temperature, and because of the corrosion difficulties with consequent low current efficiencies, this cell holds little promise for practicable fluorine production.

The medium temperature cell (70° to 110°C) was first used by Lebeau and **Damiens** who employed nickel electrodes in a system of electrolyte composition KF.3HF (8). Schumb et al (7) have made a complete study of this type of generator and report current efficiencies greater than 90 per cent and fluorine of 99 per cent purity with a melt of composition KF.(1.8 - 2.0)HF (100° to 110°C). They have shown that the nickel anodes can be replaced by ungraphitized carbon and either copper or steel can be used for the construction of the cell wall which also serves as the cathode. Polarization effects are not too troublesome and the loss of HF by evaporation can be reduced by the addition of a small percentage of LiF to the KF - HF mixture. The main difficulty encountered has been reported to be the method of attachment of the carbon plate anodes so as to ensure good electrical contact and to avoid breakage through swelling or disintegration, especially at the points of junction. These troubles arose because the connections were made in the generator gas phase and not outside the cell.

A novel design of the medium temperature cell has been produced by Burt-Gerrans, McKinnon and Rosenberg at

Toronto University and is described later in this thesis (9).

Considerable work has been done in the high temperature region which is concerned with electrolysis of a melt of composition KF.HF kept at approximately 220° to 300°C. Argo, Mathers, Humiston and Anderson first described a cell of this type (10). In later years both the design of the apparatus and the technique of operation have been improved by Simons (11). This type usually employs carbon as the anode material and copper or monel metal for the cathode which can also serve as the cell vessel. Further modifications of the high temperature generator have been made by Lossing whose design is described in detail later (12).

Although it is practicable to produce fluorine at either the medium or high temperature, present evidence indicates that the medium temperature cell is more convenient for general usage.

Sulphur Fluorides

Relatively little research has been done on sulphur fluorides, especially the lower fluorides, and any survey will, of necessity, be limited. Although the evidence for the preparation and identification of each of the gases is fairly reasonable, a great many gaps and inconsistencies still exist. The following discussion is based on a thorough historical study and represents nearly

all the information available on these compounds. The material has been presented in this section as found in the literature and any further comment on its reliability is left for the body of the thesis.

Sulphur Hexafluoride

Moissan and Lebeau first prepared sulphur hexafluoride (SF_6) by allowing solid sulphur to react with gaseous fluorine (13). It was found to be extremely stable being unattacked by water, KOH, fluorine, oxygen and hot glass. Although thermally stable up to 800°C, it was reported to decompose to Na_2S and NaF by the action of Na kept at its boiling point, and to lower fluorides by hot sulphur vapor in glass. However, Simons has passed SF_6 over sulphur at 400°C and found no decomposition (14).

The physical properties of SF_6 have been measured by many workers and have been compiled by Trautz and Ehrmann (15) in the following table (Table I). Some additions have been made by the writer.

TABLE I

Property	Value	Temp. °C	Press. mm.	Reference
Critical Point		54		Prideaux (16)
Boiling Point (sublimation)		-62	760	Prideaux (16)
		-63.8	760	Schumb and Gamble (17)
Melting Point		-55		Moissan and Lebeau (13)
		-56		Prideaux (16)
		-50.8	1710	Schumb and Gamble (17)

TABLE I (continued)

Property	Value	Temp. °C	Press. mm.	Reference
Specific Gravity	1.91	49.8	?	Prideaux (16)
Molecular Volume	76.5			Prideaux (16)
Density (cf.air) (Theor. 5.047)	5.10	20.0	755.5	Schumb and Gamble (17)
	5.03	0.0	760.0	Moissan and Lebeau (15)
Heat of Formation	262 kcals./mole			Yost and Clausen (18)
Heat of Sublimation	5.64 kcals./mole			Yost and Clausen (18)
Heat of Fusion	1.39 kcals./mole			Yost and Clausen (18)

Using electron diffraction measurements Pauling and Brockway found that the fluorine atoms in SF_6 lie at the corners of a regular octahedron and suggest that the gas has an ionic structure (19). The parachor investigations of Pearson and Robinson led them to propose that SF_6 has two covalent linkages and four semipolar singlet links (20). This is in contradiction to Sidgwick who states that singlet links are very rare and weak whereas the stability of the hexafluoride is very great (21). He postulates an expansion of the valency group to twelve which is very likely in sulphur since it has six electrons to contribute for the six links. The molecule was found to have no moment by Watson, Ras and

Ramaswamy (22).

Disulphur Difluoride

Centnerzwer and Strenck first prepared disulphur difluoride (S_2F_2) in quantity by controlled heating in vacuo of dry silver fluoride and sulphur (23,24). The gas was found to decompose easily in water to give sulphur, H_2SO_3 and HF, and in caustic to give Na_2SO_3 and sulphur which dissolved. In order to prove the identity of the new fluoride Centnerzwer and Strenck carried out quantitative analyses for sulphur and fluorine in caustic solutions in which the gas had been absorbed. Such analyses indicated the F/S mole ratio to be 1/1. S_2F_2 did not attack mercury but vulcanized rubber, and decomposed continuously for twelve to twenty-four hours on glass walls - after which time there was no further decomposition. Centnerzwer and Strenck report the melting point as -105.5°C and the boiling point as approximately -99°C.

A further study of the compound was carried out by Trautz and Ehrmann (15) who investigated many other properties of the gas although they never were able to produce a pure sample. They attributed their low molecular weights (ca.98 - theoretical 102.12), and those of Centnerzwer and Strenck, to possible decomposition of S_2F_2 into SF_2. Studies on the thermal decomposition of S_2F_2 did indicate that it broke down to give SF_2 and S. Decomposition began at 90°C and was very rapid at 200° to 350°C. Density measurements and quantitative analyses of caustic solutions in which the

gas had been absorbed substantiated these claims. S_2F_2 was found to disappear completely at 300°C, and its repugnant odor gave way to a choking smell. The gaseous decomposition products were lighter and poorer in sulphur than S_2F_2, and much more stable both to temperature and to a spark. The approximate boiling point agreed with that found for SF_2 by Ruff (-35°C).

S_2F_2 was found to be very sensitive to moisture, giving SO_2 and HF, and reacted with oxygen in the presence of a spark to give SO_2 and SOF_2.

Trautz and Ehrmann indicate that of the two possible formulae for the fluoride

$$F - S = S - F \quad \text{or} \quad S = S\begin{matrix}\diagup F \\ \diagdown F\end{matrix}$$

the second is the most likely. It is interesting to note that in the preparation of S_2F_2 these workers observed minute droplets of a colorless liquid which boiled at +50° (B.P. of S_2F_{10} = 29°).

Recent attempts to prepare S_2F_2 both at McGill and in the United States have proven unsuccessful. Although the preparation and identification by Centnerzwer and Strenck and Trautz and Ehrmann seems very accurate, the later research throws some doubt on the identification of the compound.

Sulphur Difluoride

There is only slight evidence for the existence of sulphur difluoride (SF_2). As has been mentioned, Trautz and Ehrmann postulate that SF_2 is a decomposition product

of S_2F_2 and claim to substantiate this by vapor density and analytical measurements. These workers also quote Ruff as having prepared the fluoride from the reactions of ClF and sulphur, fluorine and S_2Br_2, or fluorine and sulphur in S_2Br_2. He reported the boiling point as -35°C (15).

Sulphur Tetrafluoride

Sulphur tetrafluoride (SF_4) has been prepared by Fischer and Jaenckner by heating sulphur with cobaltic fluoride diluted with CaF_2 to prevent explosions (25). The reaction was carried out in quartz or copper since crude SF_4 attacks glass and deposits sulphur. Although mercury is attacked giving a black film. paraffin, rubber and sulphur are unaffected by the gas. Water and caustic decompose SF_4 quickly. Fischer and Jaenckner reported the boiling point as -40°C, the melting point as -124°C and the density as 3.65 (Th. 3.73). The vapor pressure of the gas was measured from its melting point to its boiling point and gave the following vapor pressure equation

$$\log_{10} P_{mm} = 7.746 - 1132.1/T$$

Simons has prepared SF_4 by allowing the vapor of sulphur monochloride to react with fluorine(14). He identified the material by a molecular weight determination (104), its boiling point (-40°C) and its melting point (-120°C), which all agreed with the values of Fischer and Jaenckner.

Thionyl Fluoride

Moissan and Lebeau first prepared thionyl fluoride (SOF_2) by the fluorination of $SOCl_2$ (26).

$$F_2 + SOCl_2 \longrightarrow SOF_2 + 2^{\circ} \text{ reactions}$$

$$2AsF_3 + 3SOCl_2 \longrightarrow 3SOF_2 + 2AsCl_3$$

The gas has a disagreeable, suffocating odor, is soluble in ether and benzene, and reacts with hot glass to give SiF_4 and SO_2. In water SOF_2 decomposes to give SO_2 and HF. Moissan and Lebeau report that oxygen reacts with the compound in hot glass to give another oxyfluoride which they did not identify.

The oxyfluoride was also prepared by Ruff and Thiel by the action of HF on S_4N_4 (27). They attributed the reaction to the presence of moisture and traces of copper oxide in the reaction tube. The compound was identified by gravimetric analyses for fluorine and sulphur and by a vapor density measurement. They gave the melting point as $-110^{\circ}C$ and the boiling point as $-30^{\circ}C$.

Booth and Mericola (28) have prepared SOF_2 by reacting SbF_3 with a refluxing mixture of 80 per cent $SOCl_2$ and 20 per cent $SbCl_5$. They measured a number of the physical and chemical properties of the gas which are listed below -

Critical Pressure	55.5 atm.
Boiling Point	-43.8°C -52°C (Moissan and Lebeau)
Critical Temperature	89°C
Freezing Point	-120° to -110°C
Vapor Pressure equation	$\log_{10}P_{mm} = 30.333 - 1908.4/T - 8.1055 \log T$
Heat of Vaporization	5202 cals/mole.

Sulphuryl Fluoride

By choosing the correct proportions of fluorine and SO_2, Moissan and Lebeau were able to prepare another oxyfluoride, sulphuryl fluoride (SO_2F_2) (29). Like SF_6, this gas is insoluble in water, stable in glass up to 500°C and is unattacked by fluorine and oxygen. Moissan and Lebeau give the following vapor pressure values

241mm. at -80°C

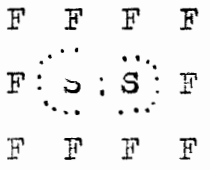
65mm. at -120°C

They report the boiling point as -52°C and the freezing point as -120°C.

Traube, Hoerenz and Wunderlich (30), and later Trautz and Ehrmann (15) prepared the gas by heating HSO_3F with BaF_2. Although SO_2F_2 is almost insoluble in dilute caustic, Trautz and Ehrmann have found that as the concentration of alkali is increased the gas becomes more soluble and at 50 per cent caustic it is completely soluble in 15 minutes (15). The decomposition is also complete with alcoholic KOH.

Disulphur Decafluoride

Disulphur decafluoride (S_2F_{10}) was first prepared by Denbigh and Whytlaw-Gray by fractionation from a sample of impure SF_6 formed from the reaction of fluorine on sulphur (2,3). They found that the gas did not react with concentrated caustic solutions and identified it by a molecular weight determination and by analysis for sulphur and fluorine after decomposition with a spark in hydrogen. The new fluoride was found to be colorless, to boil at +29° ± 1°C and to have an odor ressembling sulphur chloride or SO_2. Although unattacked by water or caustic, S_2F_{10} is decomposed by molten alkali and reacts with grease, hot platinum, cold iron, red hot copper, boiling mercury and red hot glass or silica. Denbigh and Whytlaw-Gray gave the heat of vaporization as 7000 cals./mole, the melting point as -92° ± 1°C, the Trouton constant as 23.0, the liquid density at 0°C as 2.08 ± 0.03 gm./cc. and the surface tension as 13.9 dynes/cm. ± 3%. On the basis of the surface tension measurement the calculated value for the parachor was 256 ± 4. The parachor corresponding to the formula



would be 243.

Since the discovery of the toxic effects of S_2F_{10}, considerable work has been done on its preparation and properties. At the time the writer joined F.P. Lossing on

the problem, Mungen, Hugill and Lossing at McGill had already contributed a great deal of information on both the physical and physiological characteristics of S_2F_{10}.

Mungen and Hugill prepared yields of less than one per cent by the reaction of fluorine with sulphur in a copper tube (31). These were about the same order as the best results of Denbigh and Whytlaw-Gray. No increase in yield was obtained by diluting the fluorine stream with approximately its own volume of nitrogen and then carrying out the reaction at -80°C, and in liquid sulphur.

Since the parachor values of Denbigh and Whytlaw-Gray indicated that S_2F_{10} contained an S - S link, the McGill group attempted the fluorination of S_2Cl_2, CS_2 and S_2F_2. No positive results were obtained since the S_2Cl_2 gave SF_6 but no S_2F_{10}, the CS_2 exploded and S_2F_2 could not be prepared stable enough for use. Pyrolysis of SF_6 in a quartz tube, and the reaction of hydrogen and SF_6 at 200°C using platinized asbestos as a catalyst, did not produce any S_2F_{10}. Placing sulphur and SF_6 in a closed bomb with pressures up to 100 atmospheres and raising the temperature up to 250°C was also unsuccessful. It should be pointed out here that many of these experiments were carried out at temperatures very near or above the decomposition temperature of S_2F_{10}. Fluorination of sulphur diluted with CuO, CuS and CuF_2 did not give any increase in yield. Mungen and Hugill found that S_2F_{10} was

stable in glass at room temperature but decomposed above 200°C. The presence of fluorine did not seem to hasten the decomposition. Although a large proportion of the research that follows has been done simultaneously with the McGill group, all the results obtained up to the present time are shown in order to maintain the continuity.

Alexander working in the Chemical Warfare establishment of the National Research Council found that the fluorination of sulphur diluted with solid diluents such as sodium acid fluoride ($NaHF_2$) gave increased yields of S_2F_{10}. Schneider, working in the same laboratory, found a similar general behaviour when he tried NaF, $NaHF_2$, KHF_2, KF.3HF, CuF_2 in various proportions. Although he achieved yields of 12.5 per cent by volume of the gaseous mixtures of S_2F_{10} and SF_6, his results were not duplicable and he found NaF and CuF_2 to be ineffective.

Burg, at the University of Southern California, claimed a yield of 10 to 20 per cent based on current using dilutions of 10 volumes of nitrogen to one of fluorine (32). He placed his sulphur charge in a copper reactor cooled by an air blast. The results were variable and allowed of no interpretation other than that nitrogen dilution of the fluorine stream was effective in increasing the yields of S2F10.

Burg found that the fluoride was almost completely insoluble in water and Hy-vac oil but was soluble in olive

oil to 4 per cent. The action of S_2F_{10} on charcoal gave a 44 per cent yield of SF_6, some SiF_4 and other lower fluorides. The thermal decomposition progressed rapidly in a platinum tube at 300°C at 5 - 10mm., giving SF_6 and lower fluorides which etched the glass parts of the apparatus but at 250°C the decomposition under similar conditions was extremely slow. S_2F_{10} appeared to be quite stable in contact with mild steel at 50 to 55°C. This is inconsistent with the work of Denbigh and Whytlaw-Gray and casts doubt on their statement that S_2F_{10} attacks cold iron (2,3).

Harvey and McLean have tried by various means to produce S_2F_{10} from SF_6 (33). They passed SF_6 through an electric arc with H_2S, nitrogen, and oxygen but made no S_2F_{10}. Other reduction experiments were quite unsuccessful.

Laidler at the National Research Council didn't succeed in an attempt to form SF_5 radicals from SF_6 with the intention of having them combine to form S_2F_{10} (34). Since steric factors would inhibit the collision and addition of SF_5 radicals, he suggested that S_2F_{10} would best be prepared by the fluorination of S - S links and not from the combination of two SF_5 radicals, even if they could be made. His thermal decomposition studies with S_2F_{10} in glass and copper showed that the breakdown occurred at 150°C in glass and above 200°C in copper.

J.H. Simons at Penn State has carried out a large number of separate experiments in an attempt to find a suitable method for the preparation of large yields of S_2F_{10}.

He allowed fluorine to react with a sulphur dispersion, gaseous sulphur diluted with nitrogen, the vapor of S_2Cl_2, sulphur in liquid S_2Cl_2 with iodine as the catalyst, and sulphur in CS_2 (14). Several attempts were made with fluorinating agents other than elemental fluorine. The solid but not the gaseous dispersion was found promising. The mercuric sulphide - fluorine reaction produced pure SF_6, and the S_2Cl_2 vapor - fluorine reaction relatively pure SF_4. None of the experiments which started with sulphur in a state other than S - S produced S_2F_{10}.

Huffman has made an experimental thermodynamic study of S_2F_{10} (35). He has found that the heat of formation is -460 kcals., the heat of vaporization is 6556 cals./mole, the entropy is 74.29 cals./deg./mole, and the free energy of formation of S_2F_{10} from $S_2 + 5F_2 \longrightarrow$ is -411 kcals. Pitzer, in the same paper, found the vapor pressure is given by

$$\log P_{\text{cm. of Hg.}} = -2190/T + 24.015 - 6.0 \log T$$

Disulphur Decafluoride as a Chemical Warfare Agent

S_2F_{10} has the following desirable properties as a chemical warfare agent. Its lethal index indicates a greater toxicity than any non-persistent gas now known (4)(31)(36). It is relatively inert to chemicals and heat and can be stored as a liquid at room temperature. Its low boiling point ensures a high enough vapor pressure to make dispersion rapid and simple, and the vapor is colorless and odorless in concentrations sufficient to be lethal to animals. Its high molecular weight makes for greater persistence. It is evident,

then, that S_2F_{10} behaves much like phosgene as a war gas and it is estimated to be twice as effective with a fixed expenditure of weapons (36). It should be noted that Beamish at the University of Toronto has developed oxidation-reduction indicators which are specific for S_2F_{10} if proper guard tubes are used (37).

Summary

For use as a convenient index, a number of properties of the fluorides and oxyfluorides has been assembled and is shown in Table II. Most of the data are taken from a table compiled by Trautz and Ehrmann (15). Additions have been made and the sources indicated.

TABLE II

Properties of the Sulphur Fluorides and Oxyfluorides

Property	SF_6	S_2F_{10}	SO_2F_2	SF_4	S_2F_2	SOF_2	SF_2
Odor	None	Like SO_2	None	Irritating	Disagreeable	Choking	Pungent
Action in moist air	None	None	None	Smokes	Smokes	Smokes	Smokes
Action in water	None	None	None up to 150°C	Decomposes quickly	Decomposes quickly	Decomposes slowly	Decomposes quickly
Action in caustic	None	None	Slow decomposition in mild caustic	Decomposes quickly	Decomposes quickly	Decomposes quickly	Decomposes quickly
Action of mercury	None	None	None	Attacked	None	None	None
Heat	Stable up to 800°C	Stable up to 250°C	Stable up to 500°C	?	Stable up to 90°C	Stable up to 400°C	More stable than S_2F_2
Spark	Destroyed when hot	Destroyed	Destroyed when hot	?	Destroyed	Destroyed	More stable than S_2F_2
Boiling point	-63.8°C (sublimation)	29.0°C	-52°C	-40°C	-99°C (24) -38°C (15)	-43.8°C	-35°C
Melting point	-50.8°C (17)	-92°C (2,3)	-120°C	-124°C	-105.5°C	-120° to -110°C	?

EXPERIMENTAL

The work done by the writer lends itself to division into four sections. Section I includes the techniques used and results obtained when the effect of variables on the fluorine - solid sulphur reaction was first investigated. Most of this research was done in collaboration with F.P. Lossing.

Following this work, it was decided to investigate the sulphur - fluorine system using a sulphur smoke. The changes in procedure and the resulting yields are described in Section II.

Section III shows the results found when the writer returned to the solid sulphur - fluorine system using the techniques developed for the sulphur smoke.

During this period it was found that the presence of oxygen in the fluorine stream could explain inconsistencies which had been observed in the experimental work in the first three sections. Since the oxygen originated in the fluorine generator, and since it exerted a critical effect on the yields of the various products, a medium temperature cell which produced relatively pure fluorine was installed. The modifications in procedure and results with the new cell are described in Section IV.

The analysis of results in each section is confined to a descriptive discussion. A critical analysis is then made at the end of the thesis and a mechanism suggested for the

reaction. Certain phases of the research described in the last three sections were done in collaboration with L.A. McLeod and C. Bishinsky.

As mentioned before, the fluorides and oxyfluorides of sulphur which are completely absorbed by alkali are referred to as lower fluorides (L.F.) throughout the thesis.

Section I

Apparatus and Techniques

The Fluorine Generator

(a) Description:- The first fluorine generator used by the writer was similar to that described by Denbigh and Whytlaw-Gray for high temperature fluorine production (38). The cell was first designed by J.T. Hugill, R. Mungen and R. Harvey (31) and then developed in its present form by F.P. Lossing (12)(Fig. 1).

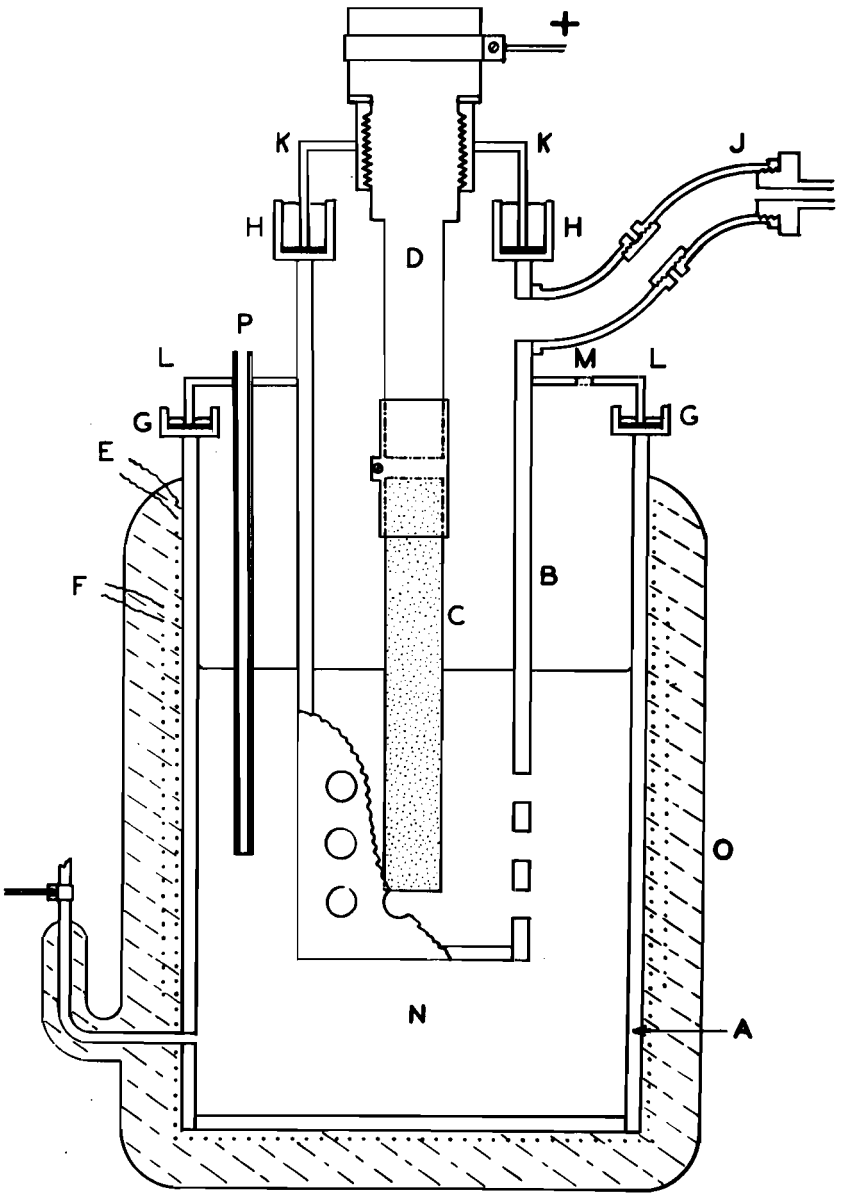
It should be pointed out here that the generator chosen for this work seemed the best available at the time. Since that time research on fluorine cells has been intensified simultaneously with the S_2F_{10} program. As a result, Schumb et al at Massachusetts Institute of Technology, and Burt-Gerrans at Toronto University have developed generators which produce far purer fluorine and are much more efficient than the cell used during the greater portion of the work at McGill.

The generator consisted of two cylindrical compartments separated by a perforated copper diaphragm. The outer cylinder or cell wall (A) was 15" deep, 8½" outside diameter, and made from 1/4" sheet copper rolled and welded. This cylinder was later replaced by a pipe of 8" diameter. The bottom of the cell consisted of the same copper material welded onto the cylinder with "low melt" welding rod.

The diaphragm (B) was made from 4½" tubing, 14" long,

Figure 1

The First Fluorine Generator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of 1/4" wall thickness and with a welded copper bottom of the same thickness. To allow for diffusion of the electrolyte, three rows of 5/8" holes were drilled around the bottom of the diaphragm.

The anode (C) found most suitable was of 1" diameter silicon-free graphite supplied by the Canadian National Carbon Co. Its mode of attachment to the copper cover of the diaphragm will be described later.

The insulation between the cathode and the diaphragm was contained in a circular trough (G) resting on top of the container. An insulating washer of transite board was laid at the bottom of the trough and since the outer trough did not have to make a gas-tight seal, a layer of solid potassium acid fluoride over transite gave satisfactory protection. The outside ring supported the cell cover (L) which, in turn, was welded to the diaphragm. A second trough (H) welded on top of the diaphragm furnished the insulation between the diaphragm and the anode. Since this assembly was always in contact with the fluorine of the anode compartment, it was necessary that the insulation be leak-proof and resistant to fluorine. After the transite washer was placed in the trough, the trough was filled with molten KHF_2 , and the diaphragm cover (K) quickly pressed into place. Solidification of the electrolyte furnished an adequate seal. The temperature at the troughs was not high enough to melt the fluoride but prevented the absorption of any excess hydrogen fluoride with consequent lowering of the melting point. These troughs were

the most important modification introduced by Lossing. They furnished insulation which would not contaminate the electrolyte and removed the mechanical strain on the insulation which had existed in the previous generators.

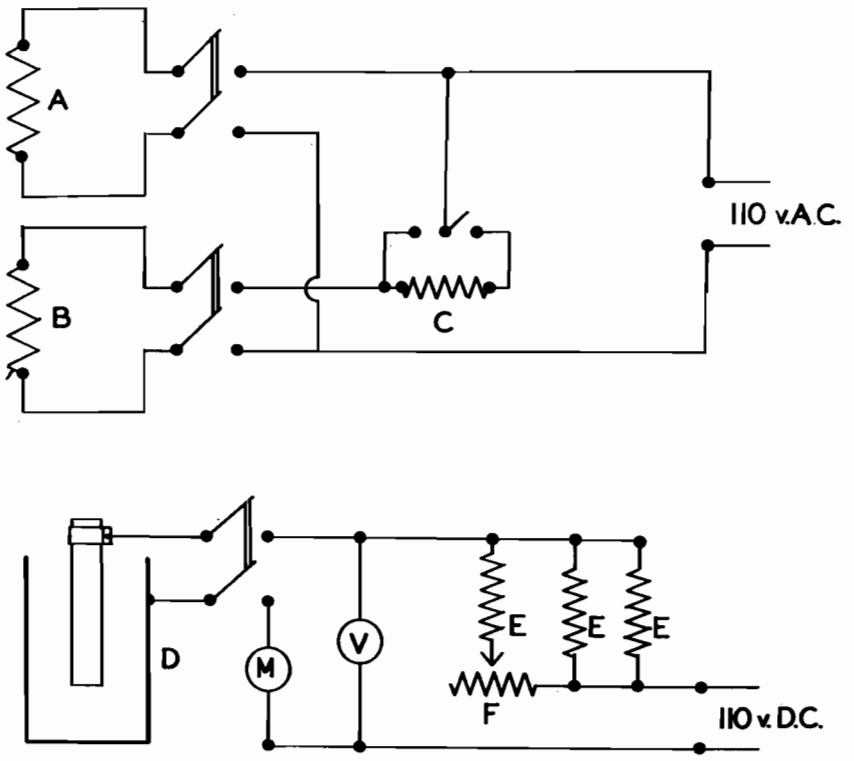
The troughs and covers were spun from 1/8" thick sheet copper. Holes were made in the cell cover (L) to allow for the escape of hydrogen (M) and to carry a length of 3/8" diameter copper tubing closed at the bottom (P). This well contained a multiple junction copper-constantan thermocouple which measured the temperature of the melt. The fluorine outlet (J) was made of two 1½" diameter copper elbows joined and welded to the anode compartment at the proper angle.

The collar of the diaphragm cover (K) was 2⅝" in diameter and was threaded to take a copper rod (D) which narrowed to 1" below the threads. The anode was fastened to the rod by a copper clamp small enough to clear the collar of the diaphragm cover. This facilitated removal of the anode assembly without disturbing the insulation. The anode projected to within 1½" of the bottom of the diaphragm.

The generator was heated by two lengths of 16 gauge nichrome wire, each drawing 10 amperes (E and F). The windings were insulated from each other and from the generator by two sheets of asbestos paper. One inch of asbestos cement completed the insulation around the heaters (O). The heating circuit is shown in Figure 2. The primary heater (A)(E - Fig. 1) contained an external resistance (C) which could be switched

Figure 2

The Generator Electric Circuit



A- SECONDARY HEATER
B- PRIMARY HEATER
C- EXTERNAL RESISTANCE

D- GENERATOR
E- RESISTANCE COILS
F- SLIDE-WIRE RESISTANCE
M- AMMETER
V- VOLTMETER

in or out. This heater ran continuously and served to keep the electrolyte near the melting point (220° - 250°C). The secondary heater (B)(F - Fig. 1) furnished auxiliary heat when quick melting of the electrolyte was required.

The D.C. electrolysing circuit (Fig. 2) was connected to the cathode through a side tube on the cell wall, and to the anode by a copper clamp. The circuit consisted of an external resistance of three 16 ohm coils in parallel (E), connected in series with an ammeter (M) and the 110 volt D.C. line. A slide wire resistance (F) in series with one of the coils allowed for any adjustments required in the current. A potential drop of ten volts was observed when 10 amperes was passed through the cell.

(b) Operation and Characteristics:- The cell charge, about 55 lbs. of potassium acid fluoride, contained waxy impurities when first melted. These floated to the surface and were removed. The cell was then electrolysed for 1 - 2 days at 10 amperes to remove the remaining impurities and any water that might be present. Actually it was found later (Section III) that this treatment did not succeed in removing all the water and subsequent electrolysis produced oxygen in the fluorine. The level of electrolyte was kept about 2" above the holes in the diaphragm.

In cell operation the concentration of HF decreased continuously because of vapor pressure loss and production of fluorine. Consequently the melting point increased, the cell

temperature had to be raised to keep the electrolyte molten, and the vapor pressure of HF increased. In order to keep the temperature in the region where the vapor loss of HF was at a minimum, it was necessary to regenerate the KHF_2 periodically by bubbling in anhydrous HF with stirring. The HF was almost completely absorbed and the melting point of the electrolyte was decreased until it corresponded to that of KF.HF. A high vapor pressure was also undesirable since the HF could then be absorbed by the insulation. This rendered the KHF_2 more or less liquid and shorting of the anode and diaphragm was observed.

The generation of fluorine did not always proceed smoothly since polarization was occasionally observed as evidenced by a jump in the voltage to 50 or 60 volts. Interrupting the electrolysis for a moment often returned the situation to normal. This polarization or voltage jump seemed to occur more frequently when the anode had begun to disintegrate. Upon removal of the anode a scale was observed on its surface. Scraping the electrode and returning it was sometimes effective.

Constant operation of the generator resulted in formation of a sludge of copper salts and pure copper in the electrolyte. The sludge had to be removed from time to time since it interfered with the proper functioning of the cell.

During these operations it was never necessary to disturb the insulating parts because removal of the diaphragm assembly permitted readjustments to be made on the cell container

or electrolyte. The diaphragm insulation lasted for about 200 hours but leaked if too much back pressure was exerted on the fluorine line. This leak could be detected with an ordinary gas burner since fluorine ignites hydrocarbon gases. If the back pressure in the fluorine generator was too large, the resulting depression of the liquid level in the anode compartment below the holes in the diaphragm allowed mixing of hydrogen and fluorine with a consequent explosion. It can be seen, then, that the leak in the insulation would have a safety valve action and no large back pressure could be built up.

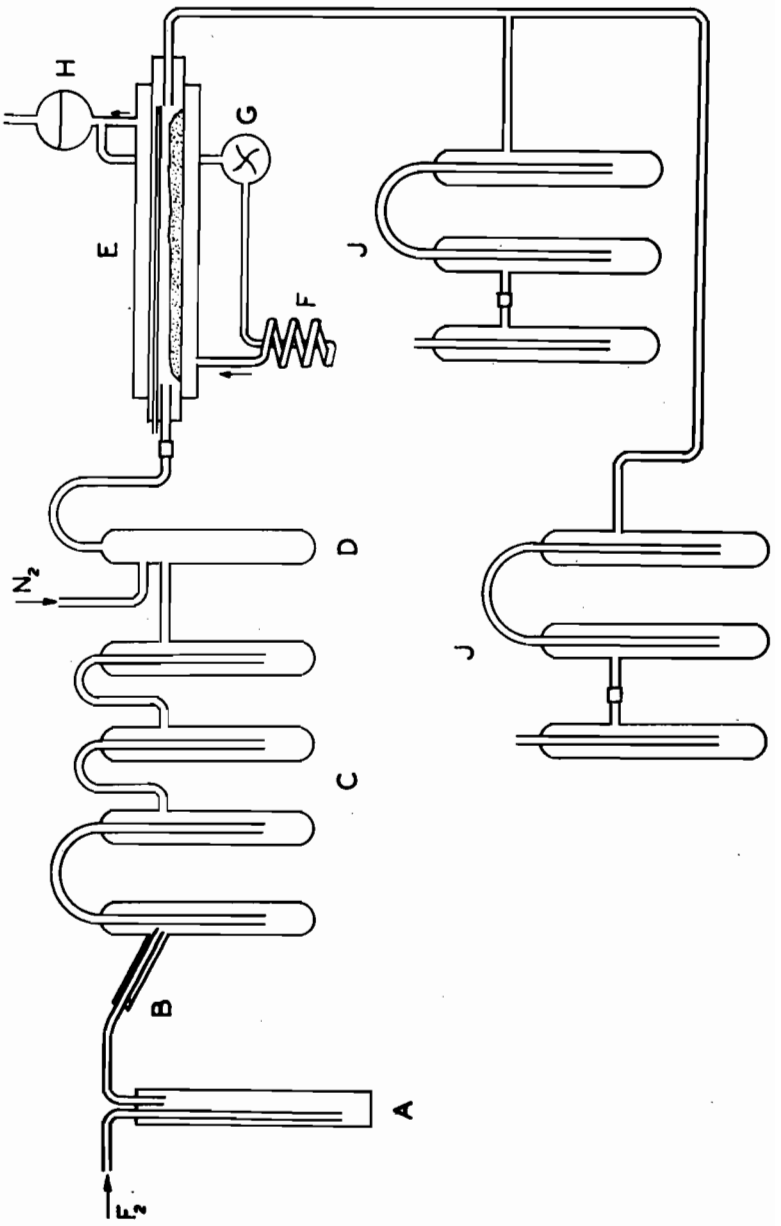
Since the experimental procedures in Section II required a completely leak-proof system, a seal was later developed for this purpose. The solid KHF_2 was covered by a layer of liquid de Khotinsky. At the temperature of the generator this baked to form a resistant film. Some fluorine did react with the de Khotinsky which necessitated renewal every twenty hours of operation.

The Solid Sulphur Reaction System

The fluorine purification train is shown in Figure 5. Hydrogen fluoride and carbon fluorides were removed by passing the fluorine through a series of traps immersed in ice and liquid air (C). The first trap (A) was made of copper and attached to the generator by a 3/8" copper tube and a series of couplings. According to literature, this trap when immersed in ice and water should have removed some of the

Figure 3

The First Reaction System


H
G
E
F
J
J
D
C
B
A
N_2
F_2

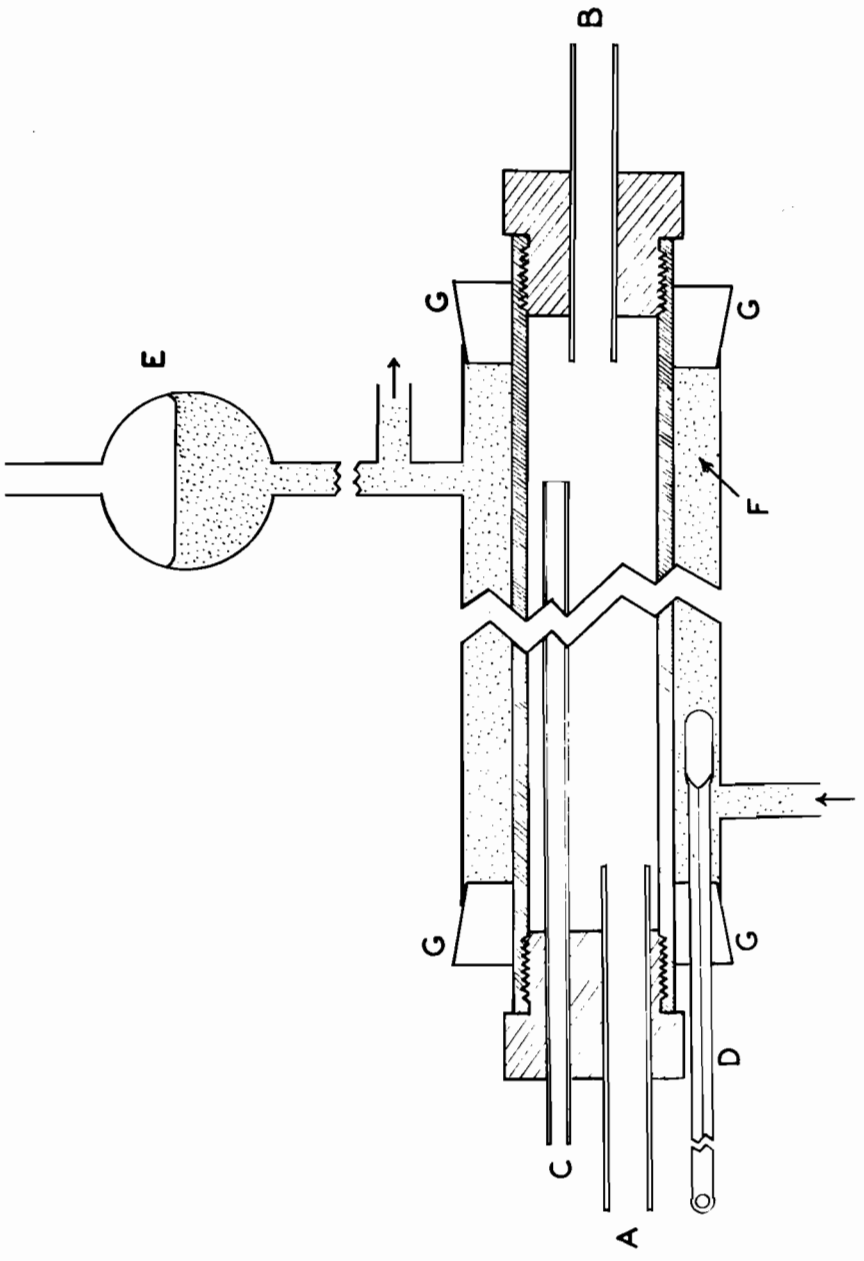
HF (B.P. +19°C). Actually it was quite ineffective and was removed for the runs in Section II (Fig. 8). A 3/8" diameter projection from the copper trap then passed into the wide side arm of the first glass trap for a distance of 3" or more. The joint at B was made leak-proof with picene. The glass traps (C) were immersed in liquid air and did remove all the HF from the fluorine stream but the first one had to be replaced periodically because of HF action.

The fluorine then passed into a mixing chamber (D) which had a supplementary inlet used for the addition of nitrogen when needed. The nitrogen was dried by passage through two $CaCl_2$ towers and two H_2SO_4 bubblers.

The mixing chamber was followed by the reaction tube (E). The first reactor used was made of one inch diameter copper tubing, 1/4" thick, 24" long, with copper plugs threaded into the ends (Fig. 4). The inlet plug contained two 3/8" copper leads (A - Fig.4) projecting a small distance into the reactor, and a small copper tube (C - Fig.4) which projected to within one inch of the outlet plug. The small tube was closed at one end and served as a thermocouple well. The outlet plug contained only one 3/8" copper lead (B - Fig.4). The reactor was first cooled by an ice bath but was later provided with a jacket through which a 50 per cent mixture of ethylene glycol and water was circulated continuously by means of an automobile water pump. The cooling was achieved by passing the ethylene glycol - water solution through a copper coil (F - Fig.3) immersed in dry ice and acetone.

Figure 4

The Solid Sulphur Reaction Tube


B
G
G
E
F
G
G
C
A
D

The temperature of the liquid in the jacket was measured by a thermometer at D (Fig. 4). During the reaction, the temperature in any part of the reaction tube could be followed by passing a copper-constantan thermocouple back and forth in C (Fig. 4). Another reaction tube of the same design but 36" long and of 1-7/8" inside diameter was used later.

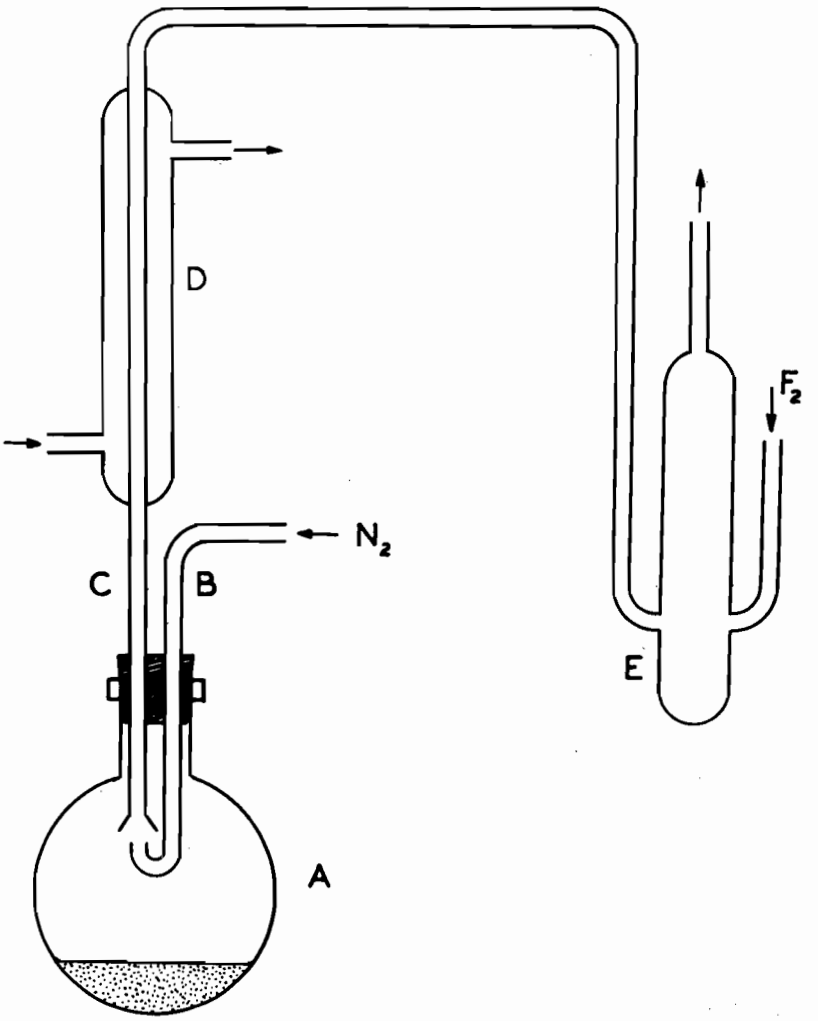
The products of reaction were collected in glass traps immersed in liquid air (J). The number of traps required varied with the volume of nitrogen used in diluting the fluorine stream. If an insufficient number of traps was used, some of the products were not condensed and were therefore lost. Large tubes were used in the traps to minimize plugging by solidified product. The body of the trap was 30 mm. in diameter and the side arm and inner tube 15 mm. in diameter. For 900 cc./min. nitrogen, at least four pairs of traps in series were required to catch all the product. The efficiency was satisfactory since mass balances on sulphur were fairly good. The glass traps were connected with double wall rubber tubing which was attacked only slowly by fluorine and lower fluorides.

The First Sulphur Smoke Reaction System

The apparatus used to observe the reaction of fluorine with sulphur smoke is shown in Figure 5. The smoke was generated in a 500 cc. Florence flask boiler (A) and was carried out at C by a stream of nitrogen which entered

Figure 5

The First Sulphur Smoke Apparatus


D
F_2
N_2
C
B
E
A

at B. The nitrogen inlet was curved upward into a small flange on the end of the outlet tube. The smoke passed through a water jacket (D) which condensed any sulphur vapor carried through by the nitrogen. It was then led into the reaction tube E, and allowed to react with fluorine which entered at another inlet. The products were condensed in glass traps immersed in liquid air.

The Analysing System

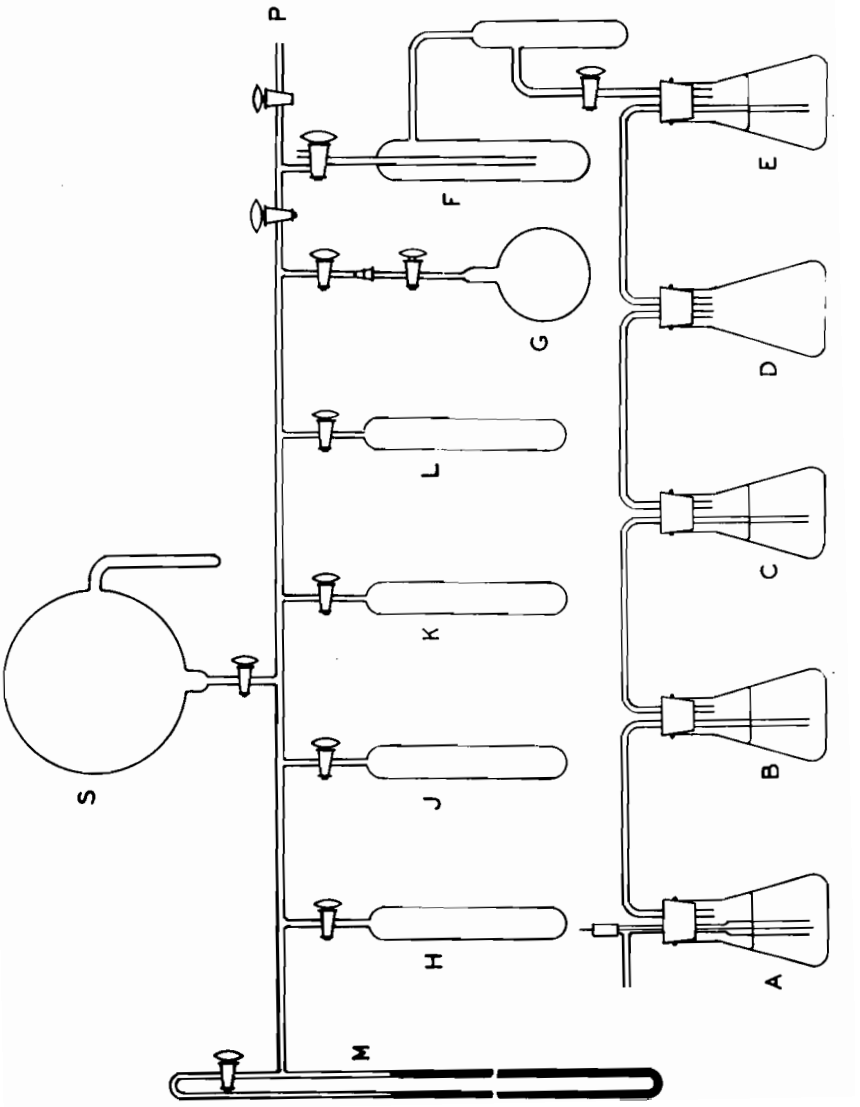
The products of the reaction were analysed in the apparatus shown in Figure 6. The SF_6 and S_2F_{10} were purified, washed, and dried by passage through two caustic bubblers (A & B), a water bubbler (C) and a sulphuric acid bubbler (E). The caustic bubblers served to remove the lower fluorides.

An ordinary delivery tube was found to plug easily in the first bubbler due to the formation of relatively insoluble material. It was then modified to include a large delivery tube and a glass rod which was used to dislodge the solid whenever any danger of plugging developed. The glass rod was held at the top of the delivery tube by a piece of rubber pressure tubing which formed a gas-tight seal and yet allowed freedom of movement. The fourth bubbler (D) served as a trap to prevent mixing of H_2SO_4 and the water - caustic series if any suck-back occurred.

The SF_6 and S_2F_{10} were condensed in the trap F immersed in liquid air. The apparatus used to analyse these gases was standard gas density equipment and consisted

Figure 6

The Analysing System


P
F
E
G
D
L
C
K
S
J
B
H
A
M

of four bulbs (H,J,K,L) for fractionation and storage, a mercury manometer (M), a gas density bulb (G) which was connected to the apparatus by a ground glass joint, a 5 litre volume (S) and a Hy-vac pump. The side tube shown on S was added at a later date and was not present for the first series of runs. The pressures were read by a cathetometer mounted in front of the manometer, and temperatures by a thermometer graduated to 0.1°C.

Procedures and Results

Preliminary Work

At the time the writer started work on this problem, a number of experiments had already been carried out on the reaction of fluorine and sulphur, which produced very little S_2F_{10}. Mungen and Lossing attributed the failure to moisture in the apparatus and in the materials (12). The first run by Lossing and the writer was carried out under dry conditions using 75 gm. solid KHF_2 and 5 gm. sulphur and resulted in a yield of 4 per cent by weight of S_2F_{10} of the gaseous mixture of S_2F_{10} and SF_6. Mixtures of the same proportions of KF and sulphur and NaF and sulphur gave yields of 10 per cent by weight. The reaction and analysing system shown and described above were then built. An experiment was done using 5 gm. sulphur diluted with 75 gm. KF and 130 cc./min. fluorine diluted with 300 cc./min. nitrogen, and a yield of 24 per cent of S_2F_{10} by weight of the gaseous mixture was obtained.

Fluorination of a Sulphur Smoke

The reaction of sulphur and fluorine is extremely energetic and exothermic. The effect of using solid and gaseous diluents for the sulphur and the fluorine indicated that heat dissipation at the point of reaction might account for the increase in yields of S_2F_{10}. Other workers attributed the effect of the solid diluent to catalysis, since the diluents used by Schneider and other workers were mainly crystalline fluorides which had the same ionic lattice. It was thought, then, that an increased yield using sulphur smoke would disprove the catalysis theory. The apparatus described on page 33 and shown in Figure 5 was used for this purpose. A stream of 300 cc./min. of nitrogen was passed through boiling sulphur and the vapors at the top of the boiler were carried in the form of a smoke through the condenser (D) and into the reactor (E). The reaction took place at the sulphur smoke inlet. The rate of smoke production was not constant and at times a faint blue luminescence was observed. This indicated a higher momentary concentration of sulphur smoke. About 9 per cent S_2F_{10} by weight of the gaseous products (S_2F_{10} and SF_6) was obtained.

The First Series

Since the preliminary runs indicated that good yields could be obtained by allowing fluorine to react with solid sulphur under controlled conditions, it was decided

to do a series of runs with this system in which the effect of variables on the yield of S_2F_{10} could be measured. This work was associated with a demand by the National Research Council for 60 gm. of S_2F_{10} for canister testing. In order to speed production and results, Lossing and the writer were joined by J.C. Arnell, J. Davis, R. Mungen and A.P. Stuart for this series of runs. The work was done in three groups of two in eight-hour shifts.

The four variables investigated included amount of gaseous diluent, amount of solid diluent, temperature and diameter of reaction tube. The reaction tube was first cooled by ice and water, but this system was later replaced by the cooling jacket shown in Figure 4. Since NaF was easy to dry and gave as good yields of S_2F_{10} as any other solid diluent employed up to that time, it was used throughout. The finely divided state of the NaF permitted intimate mixing with the sulphur.

(a) Procedure:- The charge was made up by weighing out accurately 5 gm. of dry sulphur and mixing it intimately in a mortar with the desired amount of NaF. The mixture was then placed in the reaction tube with the charge distributed as evenly as possible along the length of the tube. The reactor was weighed before and after reaction, the difference giving the amount of sulphur used. After the charged tube had been weighed, the ends were screwed on, and one of the inlets attached to the gas mixing chamber (D - Fig.3) by a

short length of rubber tubing. The other inlet was closed off and not used in this series. The outlet tube of the reactor was connected to the product traps which were immersed in liquid air, and the air removed from the system by blowing nitrogen through for a few minutes.

The generator was turned on at 10 amperes, the nitrogen set at the desired value and the time recorded. The temperature at four different positions, evenly spaced along the length of the reaction tube, was measured every half hour by the thermocouple in the narrow copper tube (C - Fig.4).

The trapping system plugged occasionally during the run due to solidification of the product in the upper part of the trap. The obstruction was melted and removed by momentarily lifting the trap out of the liquid air and warming it by hand.

During the course of the reaction, a yellow ring, probably sulphur, was often observed in the trap at the liquid air level. This disappeared when excess fluorine was passed through. No sulphur was deposited in any other part of the trapping system so it seemed clear that decomposition of one of the products was taking place. This phenomenon will be discussed later.

The reaction was allowed to proceed until the temperature at the end of the tube had fallen either to room temperature or to that of the cooling jacket. The generator was then shut off, and the products remaining in the reaction

tube carried into the liquid air trap by the nitrogen stream while the reaction tube was heated up to 50°C. This temperature was above the boiling point of any of the products and probably well below their decomposition points.

The traps were then detached from the reactor, connected in series, and the products analysed in the system shown in Figure 6. One end of the series of traps was joined to the first bubbler A, and the other end was fitted with a piece of rubber tubing and a pinch clamp. The stopcock between E and F was closed and the trap F thoroughly evacuated and then surrounded with liquid air. F was filled to atmospheric pressure with air dried by passage through the H_2SO_4 bubbler. The two way stopcock above F was then opened to the atmosphere, the pinch clamp at the end of the line of product traps closed, and the traps lifted slowly out of the liquid air surrounding them. The sample evaporated and was forced slowly through the series of bubblers by its own vapor pressure. The rate of bubbling was maintained at about 100 cc./min. by controlling the evaporation. The lower fluorides were completely destroyed by the NaOH but the SF_6 and S_2F_{10} passed through unchanged, were dried by the H_2SO_4 and recondensed in F. The last traces of product were collected by drawing air through the product traps and bubbler train by means of the Hy-vac pump for about one half hour. This operation was later changed in the following manner (Section II). The trap was immersed in hot water and nitrogen instead of air passed through for

1/2 to 1 hour. It was found that hot water hastened the evaporation and so reduced the time necessary for complete removal of the products.

The stopcock between E and F was then closed and trap F, the manifold and the small bulbs evacuated. The sample was transferred to bulb L by moving the liquid air from F to L. If any residual pressure was observed on the manometer, the system was again evacuated. The gas density was taken by expanding the sample into the manifold and large bulbs, allowing it to stand for a little while, and then filling the density bulb G. Since the volume of G was known, the molecular weight was easily calculated from the appropriate pressure, temperature and weight measurements. The gases were recondensed into L if a fractionation was desired.

Relative proportions of SF_6 and S_2F_{10} were determined from the measured molecular weight of the gas and a simple calculation yielded the weights of these gases present.

An inherent error in this method for determining molecular weights was discovered at a later time. This error arose in the method of expansion of the gases, and increased with larger amounts of S_2F_{10}. Since SF_6 has a much lower boiling point than S_2F_{10}, the first fraction of vapor contained a large proportion of SF_6 and the last fraction was almost pure S_2F_{10}. Because of its high molecular weight S_2F_{10} would diffuse slowly so that the manifold, bulb L, and the lower part of the large bulb would be relatively

rich in S_2F_{10}. Therefore, when the gas density bulb was filled it did not contain a representative sample of the gas. As a result all molecular weights done in this manner were too high, and the error varied from run to run since different lengthsof time were allowed for diffusion before molecular weights were taken.

The small bulb on S provided a method of eliminating the error. The sample which had condensed in L was again evaporated into the manifold and large bulb, but was recondensed in the small bulb attached to S. The stopcock on S was closed and the sample expanded into the bulb. Four hours were allowed for thorough mixing before molecular weights were taken. The results obtained in this manner were always consistent.

(b) <u>The Lower Fluoride Analysis</u>:- The analysis described above yielded the weight of sulphur that had reacted to give S_2F_{10} and SF_6. In order to complete a mass balance on sulphur it was necessary to determine the weight of sulphur in the caustic bubblers. This was done in the following manner.

The lower fluorides reacted with NaOH to give sulphite, sulphate and fluoride anions. It seemed simple to oxidize the sulphite to sulphate and determine the sulphur as $BaSO_4$ with $BaCl_2$. However, insoluble BaF_2 was precipitated with the sulphate. A.A. Borkovskii and N.A. Porfir'ev (39) at Zavodskaya Laboratories found that the addition of boric

acid to fluoride ion resulted in the soluble complex ion BF_4^- and so prevented the precipitation of BaF_2. They added 5 ml. of concentrated HCl and 3 gm. of $B(OH)_3$ to a 1 gm. sample of NaF containing $SO_4^=$ in 200 ml. of H_2O. The accuracy of the determination depended on the exact amounts of HCl and $B(OH)_3$ added.

The procedure found satisfactory and adopted here, then, was as follows. The solutions from the first three bubblers were made up to one litre. Two 50 ml. aliquots were taken, neutralized with HCl using phenolphtalein as indicator, and 1 ml. HCl added in excess. Five ml. of 30 per cent H_2O_2 was then added and the solutions boiled for one half hour to destroy an excess peroxide. This was necessary since peroxide interferes with the action of the boric acid. The solutions were diluted to 500 ml., 4 gm. of boric acid added, and the sulphate precipitated by 50 ml. of a 40 mg./ml. $BaCl_2$ solution. The sample was digested overnight, filtered in a sintered glass crucible, washed with 10 ml. of water and 10 ml. of acetone, dried at 105°C and weighed. The method was tested on a number of known solutions and found accurate to 5%. It was further substantiated by the mass balances obtained on sulphur.

(c) Results:- The first 27 runs were rejected since the molecular weights were obtained on unrepresentative samples (page 42). All the others in this series are listed in Table III except those rejected because of generator trouble or loss of some of the product. Some runs with low mass balances point out other items of interest and have been included. The temperatures listed in the "Temp. of

TABLE III

Generator current = 10 amperes

Run No.	N_2 c.c./min.	Tube Size in.	Sulphur Used gm.	Diluent NaF gm.	Diluent Cu gm.	Temp. of Run	% S as S_2F_{10}	% S as SF_6	% S as Lower Fluorides	Total % S
28	300	1	4.65	50		-	18.2	34.2	51.6	94.0
29	300	1	4.27	40		-	26.2	32.8	55.0	114.0
30	300	1	4.51	75		-	21.5	30.0	45.8	97.3
31	400	1	4.81	75		-	20.0	20.8	59.5	100.3
38	300	1	4.69	75		-	15.2	23.7	61.1	100.0
39	200	1	4.72	75		-	12.3	28.0	50.7	91.0
40	100	1	4.95	75		-	12.6	35.8	44.3	92.7
41	0	1	4.84	75		-	5.03	58.2	29.3	92.5
42	0	1	5.00	75		0°	3.50	33.2	25.3	62.0
43	100	1	5.00	75		0°	15.7	18.3	61.8	95.8
44	200	1	4.90	75		0°	9.65	13.4	70.0	93.1
45	300	1	4.95	75		0°	17.5	11.1	63.1	91.7
48	400	1	4.68	75		-	15.5	25.5	57.5	98.5
49	400	1	4.83	75		0°	17.2	16.0	67.3	100.5
50	300	1	4.97	75		0°	24.1	18.2	55.3	97.6
51	500	1	4.90	75		0°	14.5	15.1	67.8	97.4
52	500	1	4.34	75		-	16.7	25.0	53.3	95.0
54	200	1	4.81	75		0°	20.3	24.9	50.4	95.6
55	400	1	4.99	75		0°	18.8	18.1	64.7	101.6
56	200	1	5.00	75		-	19.9	35.1	49.5	104.4
57	200+10SF_6	1	4.86	75		-	10.7	29.2	55.9	95.8
58	100	1	4.80	20		12°	9.38	67.7	23.0	100.1
61	100	1	4.60	20		-20°	22.7	31.5	34.5	88.7
62	100	1	5.00	20		-30°	18.2	37.2	49.4	104.9
63	100	1	5.00	20		-20°	21.7	26.6	47.9	96.2
64	100	1	5.21	20		-10°	18.9	27.0	51.2	97.1
65	100	1	5.05	20		0°	18.9	48.9	29.0	96.8
66	100	1	5.02	20		-25°	22.6	9.45	63.4	95.5
67	100	1	4.37		70	-10°	26.8	26.4	50.0	103.2
68	100	1-7/8	5.05		70	-10°	22.5	25.7	53.5	101.7
69	100	1-7/8	4.88	20		-10°	22.6	20.1	53.5	96.2
70	100	1-7/8	4.90	20		-15°	25.1	16.0	42.3	83.4
71	100	1-7/8	5.00		70	-10°	28.6	23.9	48.5	101.0
72	100	1-7/8	4.81	20		-10°	25.2	22.0	53.1	100.3

Run" column are those of the outside jacket. Where no temperature is given, the reaction tube was not cooled, but left uncontrolled. A typical set of data of this series is given below.

Run 50

Charge - 75 gm. NaF and 5 gm. sulphur

Nitrogen rate - 300 cc./min.

Reaction tube used - 1 inch diameter

Temperature of run - 0°C

Weight of sulphur used (by difference) - 4.97 gm.

Time started - 1:15 A.M.

	Position			
Time	1	2	3	4
1:30	11°	8°	6°	2°
2:00	8°	10°	6°	3°
2:30	7°	9°	13°	7°
3:00	4°	8°	20°	15°
3:30	3°	3°	17°	18°
4:00	0°	0°	4°	10°
4:30	0°	0°	0°	0°

Time stopped - 4:45 A.M.

Analysis of products in gaseous mixture:

Pressure	144.9 mm.
Temperature	297.6° K.
Weight	0.7693 gm.

$$\text{Molecular weight} = \frac{R}{V}\cdot\frac{WT}{P} = \frac{119.8^{*}\times 297.6\times 0.7693}{144.9} = 189.2$$

*For convenience, the volume of the density bulb, the gas constant R = 82.07, and the atmosphere denominator 760 were compressed into the "bulb constant" 119.8.

This corresponds to 40.0% of S_2F_{10} by weight.

Weight of S_2F_{10} produced = $\frac{144.9 \times 40.0 \times 6.00 \times 254}{760 \times 100 \times 0.082 \times 297.6}$ = 4.76 gm.

Yield of S_2F_{10} (on sulphur) = $\frac{4.76 \times 64 \times 100}{4.97 \times 254}$ = 24.1%

Weight of SF_6 produced = $\frac{144.9 \times 60.0 \times 6.00 \times 146}{760 \times 100 \times 0.082 \times 297.6}$ = 4.11 gm.

Yield of SF_6 (on sulphur) = $\frac{4.11 \times 32 \times 100}{4.97 \times 146}$ = 18.2%

Weight of barium sulphate precipitate = 1.0025 gm.

Yield of lower fluorides (on sulphur) = $\frac{1.0025 \times 20 \times 32}{4.97 \times 233}$ = 55.4%

Sulphur accounted for:

24.1%
18.2
55.4
97.7%

Although inconsistent, certain general facts were indicated by the first series of runs. It was evident that nitrogen dilution raised the yield of S_2F_{10}, the gradient being greatest at low nitrogen flows (ca. 100 cc./min.). A lower jacket temperature seemed to increase the production of lower fluorides and to decrease that of SF_6. No consistent change in S_2F_{10} was observed. The larger reaction tube increased the yield of S_2F_{10}, lowered that of SF_6 and did not affect the lower fluorides to any noticeable extent. Replacing NaF by powdered copper, without changes in volume, generally raised the yield of S_2F_{10} by about 4 to 5 per cent. Since SF_6 has a higher heat capacity than nitrogen, a run was

done in which some SF_6 was mixed with the nitrogen diluent to improve heat dissipation (Run 57). This resulted in an increase in lower fluorides and a decreased amount of SF_6 and S_2F_{10}. Although runs could not be duplicated, the general changes observed in this series formed the basis for the next set of runs.

The Second Series

The first series indicated that if any accurate trends were to be observed more care would be necessary to establish uniformity of technique and analysis. The procedure was therefore altered in the next series in an attempt to reduce the inconsistencies.

(a) Procedure:- The uncontrolled manner of placing the charge in the reaction tube in the first set of runs led to an uneven distribution of the solids throughout the tube. Since little was known about the effect of such irregularities a more satisfactory method of filling the tube was developed. The charge was placed evenly in a metal trough, which was then inserted into the reaction tube, inverted, and removed.

The large weight and bulk of the reaction tubes led to inaccuracies and awkwardness in handling the charge for weighing purposes. This was simplified and standardized by reacting all the sulphur that had been weighed out accurately at the start. To ensure this, fluorine was allowed to flow through the system for one half hour after

it had reached sufficient concentration at the end of the product traps to ignite a burner.

The procedure used in starting the run was altered to maintain a constant fluorine concentration at the beginning of each run. Before connecting the reaction tube to the fluorine line, the generator was turned on, and the purification train and mixing chamber flushed free of air with fluorine. The reaction tube was then attached to the mixing chamber and the time recorded as before. The final time was taken when the fluorine reached full flow at the outlet.

(b) Results:- The results of the second series of runs are shown in Table IV. The yields on current were obtained in the following manner. In run 78, if the generator ran for 140 minutes at 10 amperes,

Amount of electricity = 10 x 60 x 140 = 84,000 coulombs.

If the generator were 100% efficient and all the fluorine reacted to form S_2F_{10}, the theoretical amount of S_2F_{10} produced would be:

$$\frac{84,000 \times 19 \times 254}{96,500 \times 190} = 22.1 \text{ gm.}$$

Actual amount produced = 4.93 gm.

$$\text{Yield of } S_2F_{10} \text{ (on current)} = \frac{4.93 \times 100}{22.1} = 22.3\%$$

As mentioned before, in this and future tables lower fluorides are represented as L.F.

TABLE IV

Generator current = 10 amperes
Reaction tube = 1 inch diameter
Sulphur used = 5.00 gm.

Run No.	N_2 cc./min.	Diluent NaF gm.	Diluent Cu gm.	Temp. of Run °C	% Sulphur as S_2F_{10}	% Sulphur as SF_6	% Sulphur as L.F.	Total % S	% S_2F_{10} on Current
76	100	75		0	14.7	53.8	35.2	103.0	11.6
77	200	75		0	20.8	36.8	40.0	97.6	16.9
78	300	75		0	24.8	23.8	53.6	102.2	22.2
79	400	75		0	23.4	22.7	51.8	97.9	21.0
80		Run spoiled							
81	100	75		-10	19.4	53.2	37.4	110.0	
82	100	75		-20	14.9	47.8	41.4	104.1	12.5
83	0	75		0	5.65	67.9	27.4	101.0	4.4
84	500	75		0	18.1	12.7	68.5	99.3	12.6
85	100	75		-30	18.1	42.6	46.7	107.4	15.1
86		Run spoiled							
87		Run spoiled							
88	100	240		0	18.0	28.5	39.8	86.3	
89	100	75		-10	20.1	46.5	39.8	106.4	15.8
90	100	75		+20	18.1	51.2	34.8	104.1	13.7
91	600	75		0	23.4	14.9	69.8	109.2	
92	100	75		-20	17.5	39.8	43.9	101.2	
93	700	75		0	18.8	10.7	69.4	98.9	
94	100	0		0	4.47	61.6	33.7	99.8	
95	600	75		0	17.5	12.1	70.5	100.1	
96	800	75		0	20.8	10.4	73.5	104.7	
97	900	75		0	10.4	12.8	72.0	95.2	
98		Run spoiled							
99		Run spoiled							
100	100	75		-10	10.7	29.3	58.9	98.9	
101	100	75		10	8.92	45.2	52.7	106.8	
102	100	75		30	10.9	53.7	40.0	104.6	
103	100	75		20	11.6	36.7	57.2	105.5	
104	100	75		10	13.2	40.2	51.8	105.2	
105	100	75		-20	13.7	48.8	36.8	99.3	
106	100	75		-10	10.9	40.1	55.0	106.0	

The results verified the trends found in the first series but were much more consistent. With increasing flow rates of nitrogen, the yields of lower fluorides increased and those of SF_6 decreased continuously up to 600 cc./min. (Fig. 7). From 600 to 900 cc./min. very little further change occurred in the yields of these two products. The S_2F_{10} increased up to a rate of 500 or 400 cc./min. and then decreased. The gradient of the curve from 500 to 900 cc./min. was in doubt since runs 95, 95 and 96 (solid line) indicated that the S_2F_{10} yield fell and then rose again whereas run 97 pointed to a general decrease (dotted line). The runs with rates greater than 600 cc./min. were in doubt because flows of this magnitude produced a large back pressure in the system with consequent leakage of fluorine at the KHF_2 insulation in the generator. A similar nitrogen series has been repeated by McLeod, Bishinsky and the writer (Section III and IV) and it has been shown that the gradual decrease was correct. However, the gradient of the curve in this region as shown in Figure 7 (dotted line) was probably too sharp.

The temperature effects were not clear and did not give distinct trends as did the nitrogen dilution. The most reliable results are collected in Table V and include some of the runs of the first series.

Figure 7

The First Results of the Effect of

Nitrogen Dilution

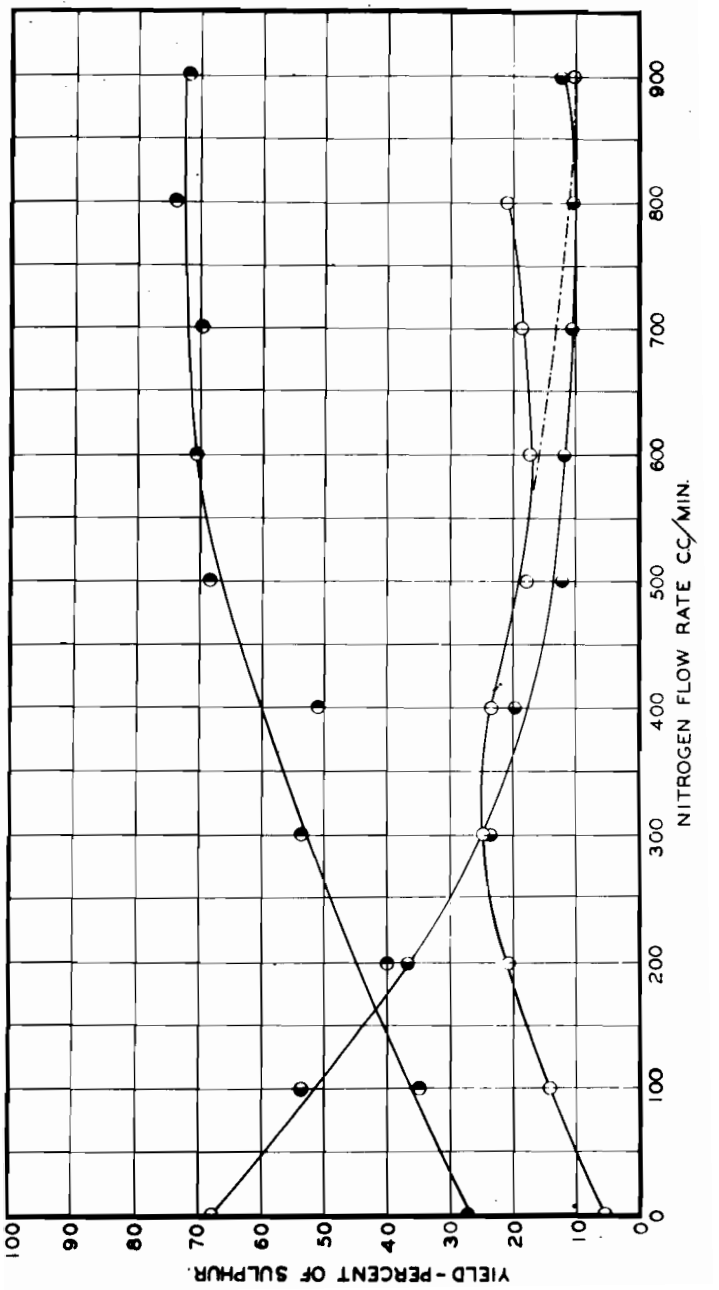

YIELD - PERCENT OF SULPHUR
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
NITROGEN FLOW RATE CC/MIN.

TABLE V

Generator current = 10 amperes
Reaction tube = 1 inch diameter
Sulphur used = 5.00 gm.
Charge = 75 gm. NaF and 5 gm. sulphur
Nitrogen flow = 100 cc./min.

Run No.	Temp.of Run- °C	% Sulphur as S_2F_{10}	SF_6	SF_4	Total % S
102	30	10.9	53.7	40.0	104.6
90	20	18.1	51.2	34.8	104.1
103	20	11.6	36.7	57.2	105.5
104	10	13.2	40.2	51.8	105.2
43	0	15.7	-	-	-
76	0	14.7	53.8	35.2	103.0
81	-10	19.4	53.2	37.4	110.0
89	-10	20.1	46.5	39.8	106.4
92	-20	17.5	39.8	43.9	101.2
82	-20	14.9	47.8	41.4	104.0
85	-30	18.1	42.6	46.7	107.4

The only trend indicated was an increase in the yield of S_2F_{10} at lower temperatures. The changes in SF_6 and lower fluorides were lost in the general inconsistencies of the results.

The effect of solid diluents is shown in Table VI.

TABLE VI

Generator current = 10 amperes
Reaction tube = 1 inch diameter
Sulphur used = 5.00 gm.
Nitrogen flow = 100 cc./min.
Temperature = 0°C

Run No.	Diluent NaF gm.	Diluent Cu gm.	% Sulphur as S_2F_{10}	% Sulphur as SF_6	% Sulphur as L.F.	Total % S
94	0		4.47	61.6	33.7	99.8
65	20		18.9	48.9	29.0	96.8
76	75		14.7	53.8	35.2	103.0
67*		70	26.8	26.4	50.0	103.2
88		240	18.0	28.5	39.8	86.3

Too few results were obtained here to observe any trends whatsoever. It did seem, however, that increased yields with solid diluent were not due to catalytic action since the crystal structures of copper and NaF were so dissimilar. The role of these compounds was probably one of heat dissipation since copper was a better diluent than NaF.

Discussion

The unpredictable variations found throughout this work were attributed in large measure to the irregular production of the fluorine generator. This would manifest itself in the unusually large time required in some runs to react five grams of sulphur.

* Run 67 was made at -10°C.

The yields based on current are lower than those based on sulphur since the generator was only 70 to 80 per cent efficient and since a large amount of fluorine was blown through the reaction tube unchanged. The best result on sulphur was 28.6 per cent obtained in run 71 with copper diluent and 100 cc./min. nitrogen. Run 78 gave the highest yield on fluorine, 22.2 per cent S_2F_{10} being obtained. The yields of S_2F_{10} on reacted fluorine were much higher. The following sample calculation on run 71 indicates the general relationship.

Weight of S_2F_{10} produced = 5.69 gm.

Weight of F_2 as $S_2F_{10} = \frac{5.69 \times 190}{254} = 4.25$ gm.

Weight of SF_6 produced = 5.44 gm.

Weight of F_2 as $SF_6 = \frac{5.44 \times 114}{146} = 4.25$ gm.

Assuming L.F. are SF_4,
% $SF_4 = 48.5$, so weight of $SF_4 = \frac{48.5 \times 5}{100} = 2.42$ gm.

Weight of F_2 as $SF_4 = \frac{2.42 \times 76}{108} = 1.70$ gm.

Total weight of fluorine reacted = 10.20 gm.

Therefore, yield of $S_2F_{10} = \frac{4.25 \times 100}{10.20} = 41.6\%$

A more complete analysis of the results has been postponed until the end of the thesis in order to present one full discussion which includes all the results obtained in SectionsI to IV.

Section II

Introduction

The results in Section I indicated clearly that S_2F_{10} could be produced in good yields by allowing fluorine to react with solid sulphur. However, certain disadvantages had arisen in using sulphur in the form of a solid bed. As the fluorine reacted with the sulphur, the ratio of solid diluent to sulphur increased and so the concentration of sulphur at any given time was not known.

Section I results also pointed to temperature control as the most important factor in producing S_2F_{10}. The dissipation of heat from solid sulphur could not be very efficient.

The addition of the sulphur in the form of a smoke seemed a reasonable method of obviating these difficulties. It had already been shown (Section I) that S_2F_{10} could be obtained from such a system. The rate of reaction could now be controlled, and the relatively small particle size of sulphur and large volumes of nitrogen would ensure adequate heat dissipation.

Apparatus and Techniques

The Reaction System

The reaction rate was regulated by variation of the sulphur smoke concentration and the rate of fluorine flow.

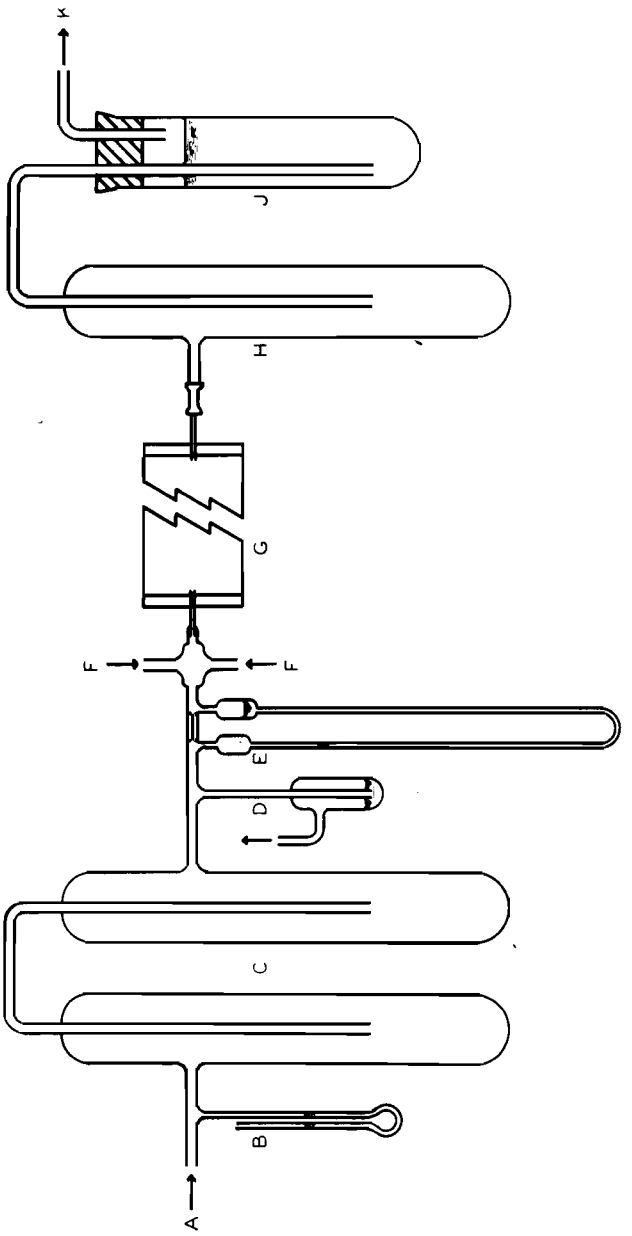
This involved the introduction of a Venturi-type flowmeter which, in turn, made many other changes necessary.

The fluorine entered at A (Fig. 8) and was again purified by passage through two liquid air traps (C). A vacuum pump was necessary at the end of the reaction train to draw fluorine through the capillary in the flowmeter which used concentrated H_2SO_4 as the liquid. This suction was especially necessary when the back pressure in the system was increased by large flows of nitrogen. Since only part of the gas flow was used, a H_2SO_4 bubbler (D) was introduced to vent any excess fluorine. A positive pressure was maintained at all times in the apparatus before the flowmeter and was measured on a sulphuric acid manometer (B).

The fluorine passed through the flowmeter and into a mixing chamber (F) with supplementary inlets for other gaseous diluents. The reaction tube (G) shown in the figure was the first of a long succession of designs used in this study and represents the same reactor used for the work in Section I. This reactor was later replaced by a glass tube of the same dimensions without a cooling jacket and with a thermocouple well through the centre of the tube. This allowed visual observation of the inside of the tube and measurement of the temperature at the point of reaction. The inlets were designed to ensure as thorough mixing as possible of the sulphur and fluorine at the point of reaction. Since the reaction only took place in the first few inches of the

Figure 8

The Modified Reaction System


K
J
H
G
F
F
E
D
C
B
A

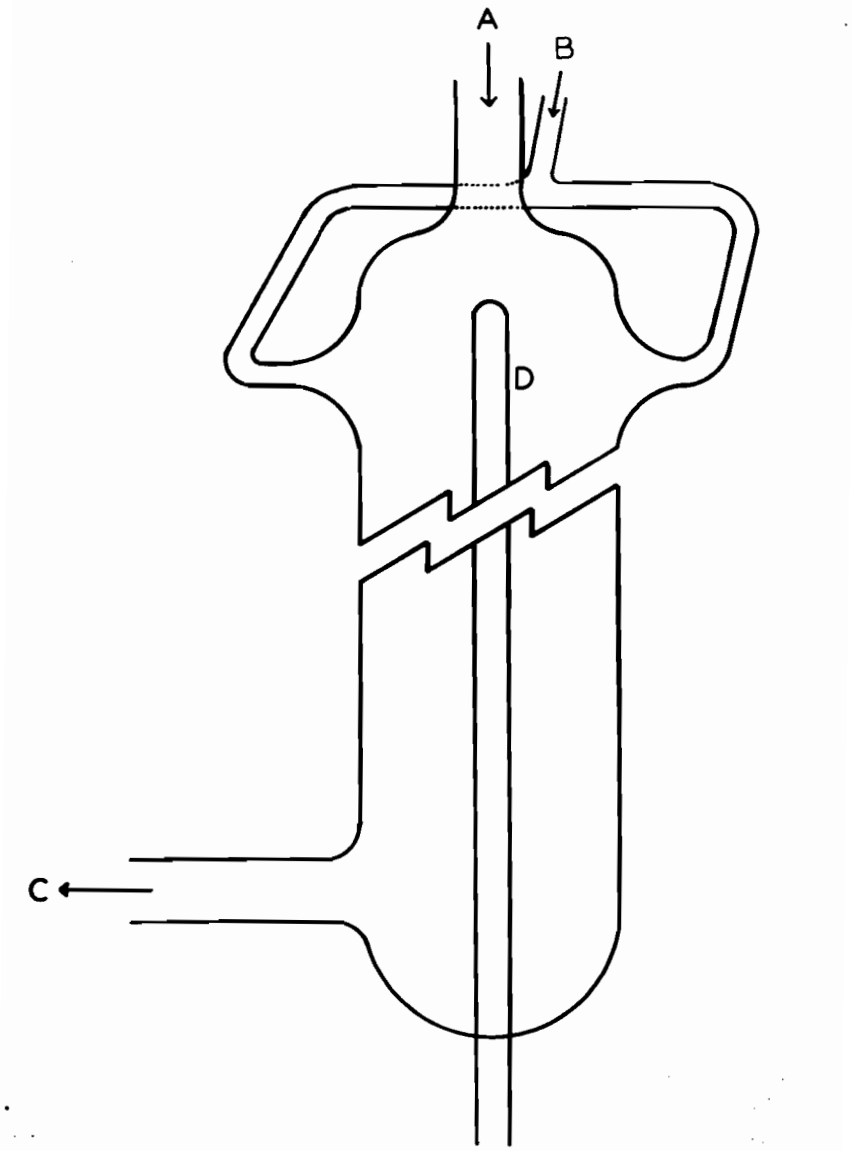
long tube, the glass reactor was redesigned into a more convenient unit. The reactor shown in Figure 9 was typical of all future tubes usedfor the sulphur smoke. Fluorine entered the one inch diameter tube at B, the sulphur smoke at A and the products were removed at C. It was found that if only one fluorine inlet was used, the reaction tended to be localized at that point and a large percentage of the sulphur settled out on the other side of the tube. The fluorine stream was therefore made to enter the reactor at two inlets which were flanged in order to ensure a wide reaction area. A thermocouple in D measured the temperature at any point in the tube. This reaction tube was 6 to 8" long and could be immersed in a dewar and thermostated.

Other modifications of this type were also employed. In one design, the tube contained a glass coil through which Prestone could be circulated continuously for cooling purposes. The reactor shown in Figure 9 was later filled with copper turnings to increase the heat conduction from the reaction zone to a constant temperature bath or vice versa. Finally, a copper reaction tube filled with copper filings was employed.

The products were first condensed in the same set of traps used in the Section I series of runs (H). However, the use of a large number of traps, dewars, and lengths of rubber tubing was found inconvenient and sometimes involved the reaction of fluorine with rubber. A trap was developed

Figure 9

The Smoke Reaction Tube


A
B
D
C

by C. Bishinsky which required only one large liquid air dewar and was efficient at least up to 900 cc./min. of nitrogen. This trap consisted of a set of vertical glass tubes of progressively diminishing diameters, joined alternately at top and bottom. The gases first passed through two 7" lengths of tubing of 1½" diameter, then 4 lengths of 3/4", and finally 2 lengths of 1/2". The large diameters were used to ensure both trapping efficiency and safety from plugging by the product. Actually, solidification of the product at one point sometimes effectively plugged the trap. Numerous modifications of this system have since been devised including traps with short horizontal rather than vertical lengths. All were designed to fit into large liquid air dewars of 3½" diameter.

The vacuum pump at the end of this reaction system necessitated the introduction of some protection behind the trap to keep fluorine from the Hy-vac pump. The bubbler shown in Figure 8 (J) was not introduced until the next series of runs (Section III). Instead, the fluorine was passed through two parallel tubes containing Na_2CO_3. The introduction of appropriate stopcocks before and after the tubes made it possible to recharge the carbonate in one tube while the other was used in the system.

The Na_2CO_3 was found satisfactory and a minimum amount of fluorine reached the pump. Passing the fluorine through NaCl and then liquid air to remove the Cl_2 worked equally well. A charcoal trap, not shown on the figure, was always placed immediately before the pump for further protection.

Sulphur Smoke Apparatus

A reproducible sulphur smoke was formed in the apparatus shown in Figure 10 by passing nitrogen over sulphur kept at constant temperature. A metered stream of dry nitrogen was introduced at A and passed through a 1 cm. spark produced by an ordinary spark coil. The spark formed nitrogen ions which furnished nuclei about which the vapor could condense thus yielding stable smoke particles and a 100 per cent increase in concentration.

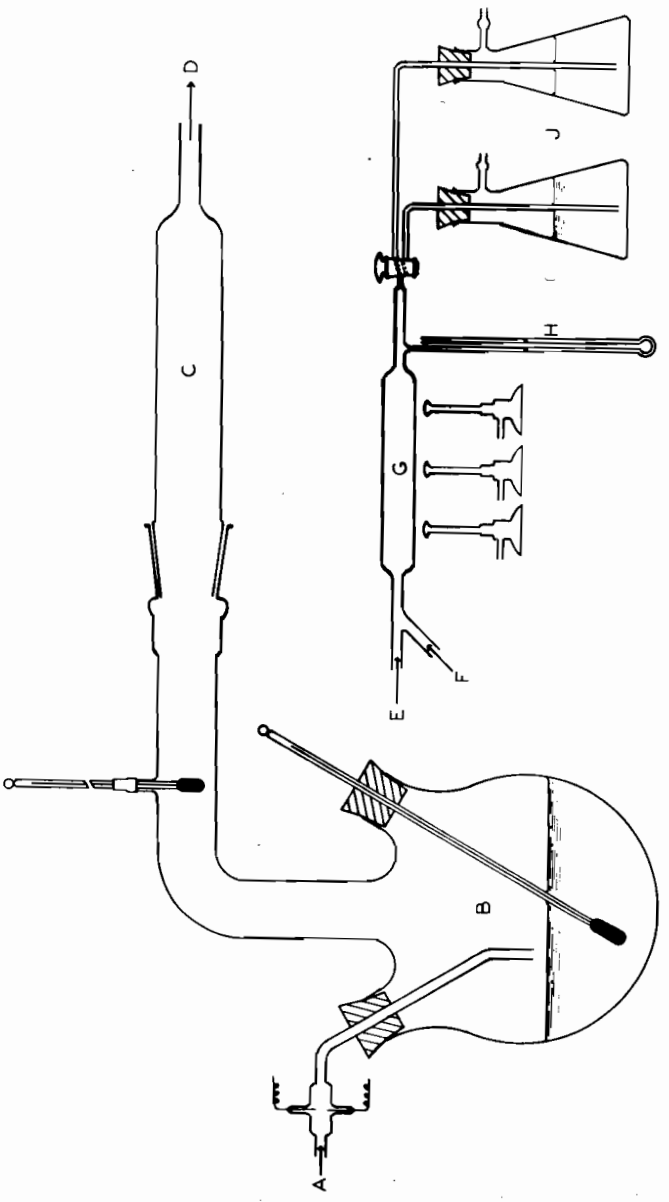
The nitrogen then passed into the sulphur boiler (B) which was heated electrically and insulated by asbestos cement. The temperature was kept constant within ± 2°C and measured by a 360°C thermometer.

The nitrogen and sulphur were heated until they reached the air condenser C. The temperature in the outlet was kept at about 50°C above that of the boiler and was also measured by thermometer. The more unstable portion of the smoke and any sulphur vapor settled out in the condenser which was removable and was connected to the generator by a ground glass joint. The smoke finally issued at D.

The concentration of the sulphur smoke was measured by pyrolysis of the sulphur to SO_2 and absorption of the SO_2 in an iodine - starch solution. A standardized iodine solution was used and the time taken for the disappearance of the characteristic blue color. Simple calculation yielded

Figure 10

The Sulphur Smoke Generator


D
C
J
H
G
E
F
B
A

the concentration of the sulphur smoke.

The smoke entered at E and O_2 was added at F. The ratio of nitrogen to oxygen found suitable was 2/1, the oxidation neither being incomplete or excessive with this volume of oxygen. The gaseous mixture was pyrolysed in a quartz tube (G) kept at red heat and was then passed through the bubblers J. It was found that when only one bubbler was used and connected to the system, a back pressure was introduced initially which altered the nitrogen rate and disturbed the equilibrium in the sulphur generator. Two bubblers were therefore used and handled in the following manner. A given smoke was pyrolysed and passed through the two way stopcock into a water bubbler. The starch - iodine solution was added to the second bubbler which contained the same amount of liquid and same diameter inlet tube. The stopcock was turned quickly to the iodine bubbler, and the time taken. The manometer (H) read the fluctuations in pressure. The final time was given by the disappearance of the characteristic blue color. The color changes were quite distinct and the accuracy good. The concentration was varied by altering either the nitrogen or the temperature of the boiler or both, and fairly concentrated and stable smokes could be obtained down to 500 cc./min. of nitrogen. The following table (Table VII) indicates the general conditions required for various sulphur concentrations. The deposit was found by weighing the condenser before and after a run and the vapor pressure was obtained from the Chemical Rubber Handbook.

TABLE VII

Sulphur Smoke Concentrations

Temp. °C	Sulphur Vapor Pressure mm.	Nitrogen Rate cc./min.	Deposit gm./hour	Smoke gm./hour	Total gm./hour	Theoretical gm./hour
200	2.1	300	0.23	0.12	0.35	0.25
		600	0.31	0.22	0.53	0.50
		900	0.36	0.35	0.71	0.74
210	3.1	300	0.32	0.15	0.47	0.36
		600	0.43	0.35	0.78	0.72
		900	0.53	0.54	1.07	1.09
220	4.4	300	0.53	0.20	0.73	0.52
		600	0.73	0.47	1.20	1.04
		900	0.74	0.75	1.49	1.55

The Analysis System

The analysis system was essentially the same as that used in Section I and shown in Figure 6. Modifications were introduced only to increase the convenience and rapidity of analyses. The water bubbler was found unnecessary and removed. A duplicate of the gas density part of the apparatus was set up and the two halves separated by a stopcock. This enabled the handling of two samples at the same time. The manometers were altered and constant volume types introduced.

The amount of gaseous product remaining after lower fluoride removal varied widely from run to run. In order to allow samples of large enough weights and pressures to be taken, a series of bulbs was added which were similar to bulb S but of capacity ranging from one half to 5 litres.

These changes ensured a higher degree of accuracy and ease in handling of the products.

Procedure

The Reaction System

The procedures used in Section I had to be altered to accommodate the changes made in the reaction system. The fluorine generator was turned on, and the system flushed free of air by passing fluorine through the train up to the flowmeter and out through the H_2SO_4 vent (D - Fig.8).

At the start of a run, the smoke apparatus and the fluorine train were both connected to the reaction tube. Since the nitrogen tended to introduce a large back pressure, the manometer first indicated a large negative value which was quickly compensated by increasing the suction.

The suction was controlled by careful adjustment of a pinch clamp placed immediately before the Hy-vac pump. The nitrogen and suction were then manipulated simultaneously throughout the run so that the fluorine and nitrogen rates were kept at the required values.

The time was recorded when the reactor was first connected to the sulphur smoke generator and the fluorine line. An excess of fluorine passing through the reaction system was quickly indicated at the carbonate tube which was sensitive to small amounts of fluorine and heated up quickly. A plug was sometimes observed in the product trap and was removed by lowering the liquid air and warming the spot where the solid had blocked the glass tube. The reaction was run until 3 - 4 gm. of sulphur had been fluorinated. The

temperature at the point of reaction was observed throughout.

The sulphur smoke generator was then detached and the fluorine generator and suction turned off. The gases remaining in the reaction tube were passed into the liquid air trap by means of a nitrogen stream with the reaction tube kept at 30°C.

Analysis

The products were then analysed, as described in Section I, only a few changes being made in the procedure. After passage through the bubblers, the gases which had condensed in F (Figure 6) were formerly analysed by a single vapor density measurement (Section I). The weight of S_2F_{10} calculated by this method was checked occasionally by separation and direct weighing. Molecular weight determinations on the residual gas samples indicated the presence of a third component of molecular weight less than 146. This was more emphatically illustrated during the sulphur smoke runs when molecular weights of the "SF_6" fraction were constantly low.

Because of the similarity in properties of this low molecular weight compound and SF_6, a separation was not feasible in the simple apparatus shown in the figure. A pure sample could therefore not be obtained for a molecular weight determination. The following method was employed in order to obtain an approximate measure of the molecular weight.

A sample of SF_6 (b) and the unknown compound (a)

was obtained by careful fractionation from S_2F_{10}, and a gas density taken on this sample. The following equation applied to any such mixture

$$\frac{P - P_b}{P} \cdot M_a + \frac{P_b}{P} \cdot M_b = M_t$$

where P = total pressure observed
P_b = partial pressure of the SF_6
M_a = molecular weight of unknown compound
M_b = molecular weight of SF_6
M_t = Molecular weight measured on SF_6 + unknown

A sample of pure SF_6 was then added to the first mixture and the molecular weight measured again. The equation then became

$$\frac{P_1 - (P_b + P_x)}{P_1} \cdot M_a + \frac{P_b + P_x}{P_1} \cdot M_b = M_{t_1}$$

where P_1 = new total pressure observed
P_x = partial pressure of the added SF_6
M_{t_1} = new molecular weight measured on SF_6 + unknown

This gave two equations, and solution for the two unknowns (P_b and M_a) yielded the molecular weight of the unknown compound. The average value obtained was 105. The only known fluorides or oxyfluorides in this region were SF_4 (M.W. - 108), SiF_4 (M.W. - 104) and SO_2F_2 (M.W. - 102). Since the first two would be removed by the caustic bubblers, the unknown compound was tentatively identified as SO_2F_2. The oxyfluoride was only slightly soluble in 10 per cent caustic

and had other properties similar to the compound described in the literature (cf. Historical - SO_2F_2). Since the vapor pressure curves of SO_2F_2 and SF_6 parallel each other fairly closely, it became obvious, then, why a simple fractionation was not possible.

Further substantiation was obtained at a later date. Since it was reported that SO_2F_2 was destroyed by alcoholic NaOH, a run in which a definite amount of SO_2F_2 was to be expected was passed through two caustic and then an alcoholic NaOH bubbler. The molecular weight of the residual gas sample, with S_2F_{10} removed, showed only the presence of SF_6. This further confirmed the claims made, unless the compound was not SO_2F_2 but was also destroyed by alcoholic NaOH. It is interesting to note that during this operation a large percentage of the S_2F_{10} is also decomposed by the alcoholic NaOH.

Assuming the presence of SO_2F_2, the analysis proceeded as follows. The total sample was condensed into one of the small bulbs (H,J,K or L - Fig.6) and surrounded by a dry ice - acetone mixture (-80°C). Since the vapor pressure of S_2F_{10} is only 2 mm. at this temperature, only the SF_6 and SO_2F_2 evaporated appreciably. The latter gases were condensed in liquid air and the separation continued until the vapor pressure above the sample was reduced to 2 mm. It was found that two successive fractionations were enough to recover all the S_2F_{10}. When pure, the S_2F_{10} was a white solid which melted near -80°C. The S_2F_{10} was then weighed and a vapor

density taken on the other fraction. Simple calculation yielded the weights of SF_6 and SO_2F_2.

Lower Fluoride Analysis

During this period, the analysis for sulphur in the lower fluorides was further modified and greater accuracy achieved. The precipitations were carried out at PH 1 to 1.5 in hot solutions and digested for one half hour while hot. The precipitate was filtered next day through Gooch crucibles rather than sintered glass. They were then washed with hot water and dried for one hour at 150°C.

At this time it was thought necessary to obtain an insight into the composition of the lower fluorides. Since all these fluorides either decompose or react with glass, separation by fractional distillation was not feasible. The weight of sulphur found from the analyses described above was of little use in itself. However a knowledge of the mole ratio of fluorine to sulphur in the caustic bubblers would give an approximate indication of the compounds involved. For instance, a ratio of 4/1 would indicate the presence of SF_4, and a ratio of 1/1, S_2F_2. Any given mixture of these two would yield an intermediate ratio. This, of course, assumed the existence of only two lower fluorides in the bubblers and would be complicated if more than two were present. It was planned to measure the effects of variables on the F/S ratio and so obtain general trends in the lower fluorides.

Various methods of analysis for the F^- ion were

therefore attempted, most of them unsuccessful because of the presence of sulphate ion and NaOH. A satisfactory procedure was finally developed by L.A. McLeod using $PbCl_2$ to precipitate both the sulphate and the fluoride ions.

After dilution of the bubbler solutions to one litre, two suitable aliquots were taken, H_2O_2 was added as before and the solutions boiled to destroy the excess peroxide. They were then made acid to methyl red and alkaline to methyl orange by adding HCl to the alkaline solution. The solutions were heated to boiling and a large excess of $PbCl_2$ was added dropwise. The combined precipitate of PbClF and $PbSO_4$ was allowed to digest overnight and filtered on Gooch crucibles. The precipitate was washed several times with saturated PbClF, once with cold water, dried for one hour at 150°C and weighed.

Since the weight of sulphur was known from the $BaSO_4$ analysis, the weight of fluorine could readily be calculated. Analyses with known solutions of F^-, $SO_4^=$ and $SO_3^=$ ions were accurate within 2 per cent. Recent evidence, however, indicates that the ratios of F/S found up to the present time have probably been incorrect, the error increasing with smaller amounts of lower fluorides in the products. It has been shown that, NaCl, formed by the NaOH and HCl in the solutions, increases the solubility of $PbSO_4$. Since a standard volume of caustic was usually used in the bubblers, the excess NaCl in the solutions would assume greater importance as the weight of $PbSO_4$ decreased. Investigations, using a method of analysis which involves the conversion of fluoride

ion to SiF_4 and consequent absorption in H_2O and titration, has confirmed these trends. Errors have been found as high as 30 per cent on the fluorine analysed.

Results

The first set of runs with the sulphur smoke were of little value since both the new reaction system and the sulphur smoke generator were in the experimental stage and did not perform consistently. Runs 1 to 30S were therefore all discarded. Runs 31 to 65S were done in the large glass reactor similar to the copper reactor (Fig. 4) and described above (Apparatus - Section II). SO_2F_2 was first identified after run 36S and subsequent runs all took cognizance of its presence. The yields of S_2F_{10} up to this time may all have been in error to varying extents.

The remainder of the sulphur smoke runs were carried out in various types of small reactors (cf. Apparatus). The results are tabulated in Table VIII and the experiments done with different reactors under different conditions are separated into groups for convenience. Many runs have had to be discarded and excluded from the table. A leak would sometimes develop before the reaction tube and air would be drawn in, nullifying the results. It was found that at very cold outside jacket temperatures, in the reaction tubes filled with copper filings, sulphur would tend to precipitate rapidly at the inlet, and either the reaction tube would plug,

or the sulphur concentration would be too low, or both. These runs were usually not analysed and are therefore not shown.

The "Temperature" column indicates the highest temperature shown by the thermocouple at the point of reaction and not that of the outside temperature jacket or dewar. Those runs which were not thermostated will be pointed out in the discussion that follows the table.

All runs were done at a flow rate of 900 cc./min. of nitrogen through the sulphur smoke apparatus. The yields were calculated on the sulphur reacted as measured by the analysis of the products.

A typical set of data for this series is shown below;

Run 85S.

Fluorine flow = 60 cc./min.
Nitrogen flow = 900 cc./min.
Temperature of sulphur boiler = 228°C
Concentration of smoke = 1.07 gm./hour
Highest temperature measured = 90°C
Time = 2 hours

Weight S_2F_{10} by weighing = 0.7790 gm.

Molecular weight on residual gas sample:

Pressure = 214.1 mm.

Temperature = 298.5°K

Total volume = 1633 cc.

$$\text{Molecular weight} = \frac{121.0 \times 298.5 \times 0.7795}{214.1}$$

$$= 131.5$$

This corresponds to 67.0 per cent SF_6 and 33 per cent SO_2F_2 by weight.

Therefore, weight of SF_6 = $\frac{67.0 \times 214.1 \times 1.633 \times 146}{100 \times 760 \times 0.0821 \times 298.5}$

= 1.84 gm.

and weight of SO_2F_2 = $\frac{33.0 \times 214.1 \times 1.633 \times 102}{100 \times 760 \times 0.0821 \times 298.5}$

= 0.632 gm.

Analysis of lower fluorides:

Weight $BaSO_4$/litre = 11.86 gm.

Weight PbClF + $PbSO_4$/litre = 51.60 gm.

Weight $PbSO_4$/litre = $\frac{303 \times 11.86}{233}$ = 15.42 gm.

∴ weight PbClF/litre = 36.18 gm.

Weight sulphur as L.F. = $\frac{32 \times 11.86}{233.1}$ = 1.628 gm.

Moles sulphur as L.F. = $\frac{1.628}{32}$ = 0.0509

Weight fluorine as L.F. = $\frac{19 \times 36.18}{261}$ = 2.580 gm.

Moles fluorine as L.F. = $\frac{2.580}{19}$ = 0.1360

F/S ratio = $\frac{0.1360}{0.0509}$ = 2.67

Weight sulphur as lower fluorides = 1.628 gm.

Weight sulphur as SF_6 = $\frac{32 \times 1.84}{146}$ = 0.403

Weight sulphur as S_2F_{10} = $\frac{64 \times 0.7790}{254}$ = 0.195

Weight sulphur as SO_2F_2 = $\frac{32 \times 0.632}{102}$ = 0.198

Total weight sulphur reacted = 2.426 gm.

Per cent sulphur as

Lower fluorides	= 67.1%
SF_6	= 16.6
S_2F_{10}	= 8.0
SO_2F_2	= 8.3
Total	=100.0%

TABLE VIII

Sulphur Smoke Results

Nitrogen rate = 900 cc./min.

Run No.	Fluorine Rate cc./min.	Sulphur Conc. gm./hour	Temp. °C	Sulphur Reacted gm.	L.F.	% Yield on Sulphur SF_6	S_2F_{10}	SO_2F_2	F/S Ratio
Group 1									
31S	90	1.07	150	4.27	58.5	59.8	1.9		2.19
52S	60	1.07	120	4.80	43.5	53.2	3.5		2.20
36S	40	1.07	95	4.05	73.8	17.3	8.9		2.55
33S	30	1.07	75	3.44	83.8	10.2	6.1		2.36
35S	15	1.07	55	2.90	67.5	21.0	11.4		2.86
Group 2									
56S	60	0.50	65	2.06	70.3	18.7	7.7	3.4	2.46
50S	30	0.50	75	3.39	77.0	12.7	7.0	3.4	2.43
52S	15	0.50	55	2.31	94.4	1.3	1.1	3.4	2.46
Group 3									
59S	60	0.25	50	1.62	83.5	7.6	3.3		2.57
60S	60	0.25	125	4.40	69.7	18.0	4.4	7.8	2.72
61S	60	0.25	200	1.14	50.2	32.6	4.5	12.7	3.06
57S	10 - 15	0.25	50	1.21	77.8	11.8	6.3	3.9	2.24
62S	10 - 15	0.25	200	1.44	65.6	22.4	5.8	6.1	1.92
63S	10 - 15	0.25	310	1.47	50.0	36.5	4.3	9.0	3.19
Group 4									
68S	60	1.07	20?	2.96	70.4	15.9	9.8	3.9	2.47
74S	60	1.07	100	1.84	70.1	17.1	9.2	3.6	2.16
67S	60	1.07	140	3.12	64.5	23.2	10.6	1.8	2.48
69S	60	1.07	250	2.54	41.0	50.0	5.9	2.9	2.84
70S	60	1.07	400	2.09	71.8	25.8	1.0	1.2	3.94

TABLE VIII (continued)

Run No.	Fluorine Rate cc./min.	Sulphur Conc. gm./hour	Temp. °C	Sulphur Reacted gm.	% Yield on Sulphur L.F.	SF_6	S_2F_{10}	SO_2F_2	F/S Ratio
Group 5									
80S	30	1.07	20	1.51	71.4	16.0	9.5	3.2	1.60
77S	45	1.07	20	2.21	69.9	19.2	6.0	4.9	1.47
76S	60	1.07	20	2.28	67.6	20.1	4.9	7.4	1.98
79S	75	1.07	20	2.19	57.3	29.7	7.2	5.7	2.59
78S	90	1.07	20	2.11	51.4	33.3	5.9	9.5	2.10
Group 6									
85S	60	1.07	90	2.43	67.1	16.6	8.0	8.2	2.67
91S	60	1.07	85	2.21	67.0	18.7	5.6	8.8	
86S	60	1.07	200	1.71	48.0	39.1	7.2	5.8	2.03
87S	60	1.07	300	1.73	38.8	44.8	1.8	14.5	2.14
88S	60	1.07	400	0.99	37.8	10.4	0.7	50.3	0.80

Discussion

Although many of the trends were not distinct, the results are discussed here in a qualitative manner. As in Section I, an analytical treatment has been postponed until the General Discussion.

The first group of runs (Group 1), in the long glass reactor, represent the changes observed when the fluorine rate is varied at a constant sulphur smoke concentration. Lower fluorine rates resulted in an increase in the yield of lower fluorides, a decline in SF_6, and, in general, an increase in S_2F_{10}. This same variation was repeated in the same reaction tube using half the concentration of sulphur smoke (Group 2). Duplicate trends were observed in the SF_6 and lower fluorides but the S_2F_{10} yields were not consistent, the amount falling off sharply at 15 cc./min. fluorine (Run 52S). No temperature control was attempted in all the above runs so that the effects observed could not be attributed solely to the fluorine variations.

In Group 3, the sulphur concentration was halved again ($\frac{1}{4}$ gm./hour), and the temperature varied at two different fluorine rates. The reactor was heated electrically by nichrome wiring wound around the outside of the tube and controlled so that the desired temperature was still obtained in the thermocouple well. In both instances, an increase in temperature led to an increase in SF_6 and a decrease in lower

fluorides and S_2F_{10}. The changes in S_2F_{10} were small, however, relative to the changes in SF_6 and lower fluorides. This indicated that macroscopic temperature effects might not be an important factor in S_2F_{10} production.

The small reactor containing the glass coil in the inside of the tube was used for the Group 4 series of runs. For the lower temperature the reactor was cooled by circulating cold Prestone through the coil. Nichrome wiring was used for heating purposes. At constant fluorine and sulphur concentrations, the increase in temperature resulted in distinct trends up to 250°C, similar to those observed in Group 3. Two explanations can be offered for the sharp breaks observed in run 70S. At higher temperatures fluorine attacks glass to give SiF_4 and sulphur oxyfluorides which would be absorbed by the bubblers and show up as lower fluorides. All the fluorine could therefore have appeared as lower fluorides rather than SF_6 or S_2F_{10}. The sharp jump in the F/S ratio would tend to substantiate this. The claim of Moissan and Lebeau (13) that hot sulphur vapor and SF_6 react in hot glass to give lower fluorides may be another plausible explanation although Simons (14) has disputed this work (cf. Historical - SF_6).

The Group 5 runs were done with the reactor shown in Figure 9 but filled with copper turnings. An increase in fluorine at constant temperature and sulphur concentration resulted in the same trends observed in Group 1, namely, an increase in SF_6 and decrease in lower fluorides and S_2F_{10}.

The trends in S_2F_{10} were again not as distinct as the other two.

Since it was thought that the results of temperature variation found in the glass reactor were obscured by the possible reaction of glass and fluorine at higher temperatures, this series was repeated using a copper reactor of the same design as that shown in Figure 9 and filled with copper turnings (Group 6). The general increase in SF_6 and decline in lower fluorides and S_2F_{10} was again observed up to 300°C. Since the decomposition temperature of S_2F_{10} lies in the region of 250 - 300°C, the reason for the S_2F_{10} decrease at high temperatures was obvious. Numerous factors could account for the sharp decrease in SF_6 at 400°C in run 88S. The small change in lower fluorides would indicate that not much decomposition of SF_6 to lower fluorides had occurred. However, the high temperature at which this run was done resulted in a number of changes in the reaction conditions themselves. The rubber connections to the copper reactor were hot and could have reacted to give carbon fluorides. If these fluorides did not react with NaOH, a small amount in the gas density system, could decrease the molecular weight significantly and give false values for the weight of SF_6 and SO_2F_2. It was also found that copper reacted with both fluorine and sulphur at this temperature, so that the concentration of the variables could not be ascertained. The result is really of little significance since the general trends are indicated up to 300°C.

In all this work no attempt was made to draw positive conclusions from the results of one run. The trends were not distinct and could not be evaluated in their proper perspective until verified later with far greater accuracy by the runs discussed in Section IV.

The fluorine - sulphur ratio has not been mentioned significantly in this discussion since it is believed that the inaccuracies in the fluorine analysis completely prevent any positive conclusions to be drawn.

Section III

Introduction

With the development of the new reaction and analysis system used in the sulphur smoke experiments, it was now possible to investigate a wide range of conditions with greater accuracy. Although inconsistencies were often observed, the yields of S_2F_{10} were generally of the order of 5 to 10 per cent on sulphur. This was low compared with the amounts of S_2F_{10} obtained when fluorine was allowed to react with a solid bed of sulphur. Further research with the smoke might have given a clearer insight into the mechanism of the sulphur - fluorine reaction, but the low yields were undesirable from a commercial viewpoint. It was therefore decided to forego theoretical investigation with the sulphur dispersion and re-examine the solid system using the new techniques and apparatus.

It has been shown in Section I that the sulphur concentration in a solid bed could be varied by addition of solid diluent. The rate of reaction could now be controlled further by the variation in fluorine flow. Since use of suction eliminated back pressures, the nitrogen changes could be reinvestigated without limit and the effect of larger dilutions determined more accurately (cf. nitrogen dilution - Section I).

As has been mentioned, research up to this time

indicated that production of large amounts of S_2F_{10} required the use of nitrogen diluent. This method of preparation was not feasible on a commercial scale because of the difficulties involved in handling a gas like nitrogen which was so difficult to condense. A search was therefore made for a higher boiling gas, inert to fluorine, which would replace nitrogen. Dichlorotetrafluorethane (sold under the trade name "Freon 114" by Kinetic Chemicals Ltd.) which boils at 4°C was thought to fill these requirements. Since all previous work indicated that the diluents exerted a thermal effect, Freon had the further advantage of higher heat capacity compared to nitrogen. Less gaseous diluent would therefore be required to produce comparable increases in the yields of S_2F_{10}.

Apparatus and Techniques

Only slight changes were made in the apparatus described in Section II. Since a method of analysis for fluoride in the caustic bubblers had been developed, and since the fluorine could be metered accurately, it was now possible to follow the fluorine as well as the sulphur balance. This necessitated complete reaction of any fluorine that entered the reaction tube.

The charge was made up as before but 10 rather than 5 gm. of sulphur was used. If only 3 to 4 gm. was reacted, an excess of sulphur was ensured, and if the nitrogen dilutions

were not too great, the fluorine did not pass the sulphur bed unchanged. The 1" reactor was again employed in this work but it was filled in a different manner. The solids were now distributed evenly in a copper trough which was then inserted into the reaction tube. The amount of sulphur used was found by weighing the boat before and after reaction.

It was found that if nitrogen dilutions were used, some fluorine did pass through the reaction tube. A KI bubbler (J - Fig.8) was therefore introduced after the product trap to absorb the unchanged fluorine. Titration, with standard AS_2O_3, of the iodine formed yielded the weight of fluorine. Since the bubbler served to remove any excess fluorine before the gases reached the Hy-vac pump, the carbonate tubes were removed for all consequent experiments.

Results and Discussion

The First Series of Experiments

No results were obtained with Freon. Several attempted experiments with varying dilutions were unsuccessful since an explosion always occurred before enough products could be collected for analysis. These explosions took place even if sulphur was not present and indicated that the Freon - fluorine mixture was responsible. Since later work showed the presence of oxygen in the fluorine stream, it was possible that the reactions were initiated by the impurity and that the pure gases would not explode. No other work has since been done in this direction.

Following the unsuccessful attempts with Freon, it was decided to re-examine the nitrogen dilution and to investigate the effects of other variables. The results are shown in Table IX. No fluorine balances were obtained until run 10A when the KI bubbler was first installed.

Runs 6 to 13A and 16A show the variation in yields with increased nitrogen dilutions (Fig. 11). The yields and trends observed followed the same general behaviour found by Lossing and the writer in Section I (cf. Table IV and Fig. 7). The SF_6 yields decreased and the lower fluorides increased, and then both levelled off sharply, whereas that of S_2F_{10} passed through a maximum. At first glance it might appear that the gradient of the S_2F_{10} curve was again in doubt beyond the maximum value. However, closer examination of the results indicate that the S_2F_{10} yield in run 9A was probably incorrect. Although the values of SF_6 and lower fluorides were duplicable at these higher flow rates of nitrogen, the amounts of both these products were inconsistent with the general trends. The S_2F_{10} curve has therefore not been drawn through this point (9A) and a gradual decline in yield has been shown at nitrogen dilutions greater than 800 cc./min. Further justification for this representation will become evident later in both the experimental results and discussion.

An attempt was also made to examine the effects of solid diluent, temperature, and fluorine rate, in the absence of nitrogen. Although no trends were observed, these

TABLE IX

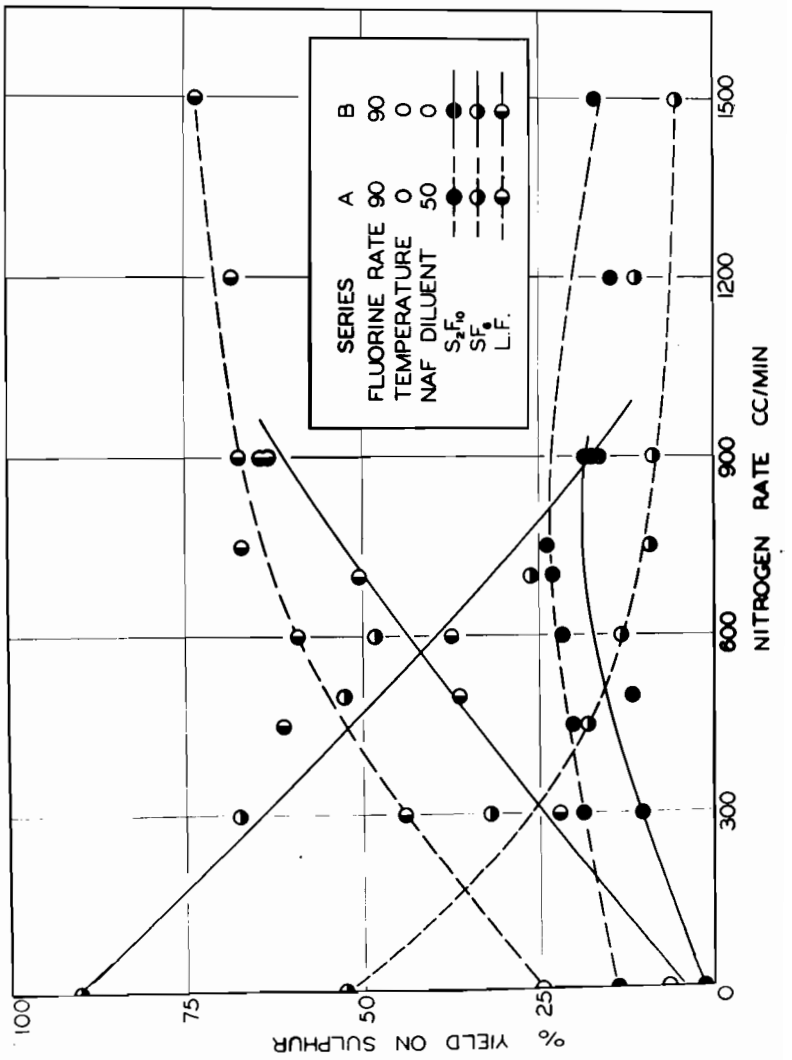
Series A

Weight sulphur in charge = 10 gm.

Run No.	Fluorine cc./min.	Nitrogen cc./min.	Wt. NaF gm.	Temp. °C	Sulphur Reacted gm.	% Yield on Sulphur L.F.	SF_6	S_2F_{10}	SO_2F_2	% Yield on Fluorine L.F.	SF_6	S_2F_{10}	SO_2F_2	F/S Ratio
10A	90	0	50	0	3.28	23.4	54.5	13.2	8.9	8.5	72.9	14.6	4.0	1.66
6A	90	300	50	0	4.84	43.5	31.5	18.0	7.1					2.43
11A	90	450	50	0	4.12	58.9	17.4	19.4	4.4	43.1	24.6	22.8	2.1	3.12
7A	90	600	50	0	4.68	57.3	13.6	22.4	6.7					2.73
12A	90	750	50	0	4.23	65.0	8.9	22.9	3.3	46.0	12.5	21.0	1.6	3.00
8A	90	900	50	0	3.93	66.0	9.0	17.0	8.0					3.47
16A	90	900	50	0	3.36	69.0	8.7	17.9	4.6	46.1	10.5	18.1	1.8	3.30
9A	90	1200	50	0	3.64	67.9	10.9	14.2	7.0					3.86
13A	90	1500	50	0	4.40	74.8	5.9	17.3	2.0	42.9	7.3	18.0	0.8	2.83
14A	30	0	50	0	2.23	36.4	31.4	17.3	14.8	24.4	46.6	21.6	7.3	2.73
18A	45	0	50	0	3.58	42.8	30.0	11.9	15.4	22.1	51.7	17.3	9.0	1.80
25A	45	0	50	0	1.96	32.2	38.2	14.8	14.8	21.6	54.0	17.6	6.9	2.86
15A	60	0	50	0	4.96	24.3	42.6	22.4	10.7	16.1	55.0	24.2	4.6	3.08
30A	60	0	50	0	3.15	22.6	55.5	10.8	11.2	10.6	72.4	11.5	4.8	2.37
36A	60	0	50	0	3.41	24.1	58.4	6.8	10.9	14.2	74.0	7.2	4.6	2.82
17A	75	0	50	0	5.20	41.0	31.2	5.4	22.5					2.60
24A	75	0	50	0	4.19	30.4	60.2	4.1	5.5	21.4	72.5	4.1	1.9	3.51
10A	90	0	50	0	3.28	23.4	54.5	13.2	8.9	8.5	72.9	14.6	4.0	1.66
27A	60	0	0	0	3.52	28.1	55.7	2.3	13.9	16.6	74.5	2.7	6.3	3.46
26A	60	0	25	0	3.70	31.7	49.4	4.1	14.9	19.3	69.1	4.7	6.9	2.69
23A	60	0	100	0	3.94	46.0	28.2	7.4	19.5	32.5	47.0	10.3	10.2	2.55
34A	60	0	50	-20	2.94	18.4	64.4	9.9	7.8	10.2	76.8	10.0	3.2	2.78
32A	60	0	50	50	2.94	19.1	64.3	4.8	11.9	10.6	79.8	4.9	4.9	2.68
33A	60	0	50	75	2.97	12.1	70.4	5.7	11.8	5.8	84.2	5.5	4.6	2.28

Figure 11

The Effect of Nitrogen Dilution in Series A and B


SERIES A B
FLUORINE RATE 90 90
TEMPERATURE 0 0
NAF DILUENT 50 0
S_2F_{10}
SF_6
L.F.
% YIELD ON SULPHUR
0
25
50
75
100
300
600
900
1200
1500
NITROGEN RATE CC/MIN

experimental results have been included in the table and show the wide variations encountered in this system.

Effect of Oxygen

These inconsistencies persisted even though apparently identical reaction conditions were maintained. A careful review of all the data was therefore made in an attempt to find an explanation for the variable results.

It was noticed, especially in the smoke runs, that even when trends were sometimes obtained with lower fluorides and SF_6, the fluctuations of S_2F_{10} persisted. These inconsistencies could either be due to errors in the analysis of the products or to lack of reproduction of reaction conditions. A review of the analytical procedures showed that the variations were too large to be accounted for in this manner.

However, a possible source of error did exist in the reaction system. A rough analysis had shown the presence of some impurity in the fluorine stream. Moreover, in nearly all the runs in Sections II and III, SO_2F_2 had been found in the products. It was observed that a rough correlation existed between the amount of SO_2F_2 produced and the yield of S_2F_{10}. Although no trends were noticed in either of these two products, an increase in the amount of SO_2F_2 was usually accompanied by a decrease in S_2F_{10} yield. This was particularly

evident when a leak had occurred before the reaction tube and air was drawn into the reaction zone. These runs would invariably require repetition because of low S_2F_{10} yields. Since the inconsistencies persisted with a leak-proof system, a variable amount of some impurity, probably oxygen, in the fluorine stream was suspected as the source of the trouble.

Analysis of the fluorine showed the presence of approximately 35 per cent oxygen, although later work indicates that this value was probably too high. The analysis was carried out in a gas analysis system, the fluorine being determined by absorption in KI and the oxygen by absorption in pyrogallol. Fluorine samples which gave 70 to 80 per cent fluorine and over 20 per cent oxygen with this system have been found to contain more than 95 per cent fluorine by an analysis with mercury. However, it is known that oxygen was undoubtedly present since the percentage of fluorine was comparatively low, and for other reasons which will become evident later.

To show that the formation of S_2F_{10} was being inhibited by oxygen, a series of experiments were carried out in which known amounts of oxygen were added to the fluorine stream (Table X).

TABLE X

Effect of Oxygen

Fluorine rate = 60 cc./min.
Weight of NaF diluent = 50 gm.
Temperature = 0°C

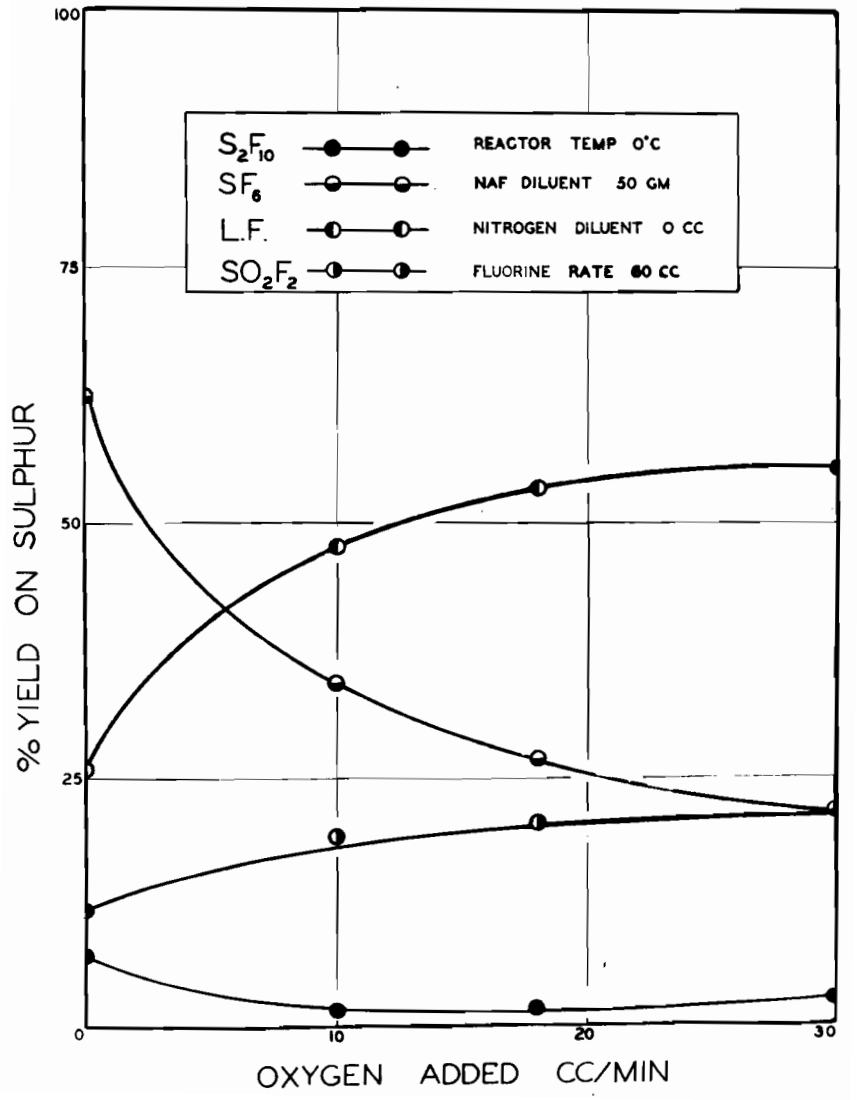
Run No.	Nitrogen cc./min.	Oxygen added cc./min.	% Yield on Sulphur L.F.	SF_6	S_2F_{10}	SO_2F_2	F/S Ratio
36A	0	0	24.0	58.4	6.8	10.9	2.82
38A	0	10	46.4	33.4	1.5	18.8	2.15
39A	0	18	52.0	26.4	1.8	19.9	2.46
40A	0	30	54.9	21.4	2.6	21.1	2.31
41A	300	10	72.6	14.3	8.2	4.8	2.26

The results are illustrated graphically in Figure 12. As anticipated, it can be seen that increased oxygen led to a sharp increase in SO_2F_2 accompanied by a corresponding decrease in yield of S_2F_{10}. Both curves levelled off at the same point. It is also interesting to note the changes in the other two products. The production of SF_6 was inhibited as much as the S_2F_{10}, and the yield of lower fluorides increased rapidly. It seemed, then, that the presence of oxygen increased the yield of lower fluorides at the expense of the SF_6. This increase in lower fluoride yield could have been due to the formation of another oxyfluoride which was absorbed in the caustic bubblers.

An attempt was also made to determine the effect of oxygen in the presence of nitrogen. If runs 6 and 41A are compared, it can be seen that 10 cc./min. of oxygen in the presence of 300 cc./min. nitrogen did not affect the yield of SO_2F_2 but the lower fluorides increased markedly.

Figure 12

The Effect of Oxygen


100
75
50
25
0
10
20
30
% YIELD ON SULPHUR
OXYGEN ADDED CC/MIN
S_2F_{10}
SF_6
L.F.
SO_2F_2
REACTOR TEMP 0°C
NAF DILUENT 50 GM
NITROGEN DILUENT 0 CC
FLUORINE RATE 60 CC

Since the yields of SF_6 and S_2F_{10} both decreased, it seemed again that the amounts of these compounds were associated with the yields of SO_2F_2 and some compound in the lower fluorides, presumably SOF_2.

It is also interesting to compare runs 38 and 41A in which the effect of 300 cc./min. nitrogen in the presence of 10 cc./min. oxygen is shown. The increase of S_2F_{10} was not as rapid as usual but a change from 2 to 8 per cent was observed. It would seem, therefore, that although oxygen did exert some poisoning action, its effect was not as critical as before. If the volume of oxygen originally present in the fluorine stream was not too large, this would explain to some extent the relatively consistent trends found in the presence of nitrogen. This is particularly true at higher nitrogen dilutions where the same volume of oxygen is even less significant. These experiments will be discussed in greater detail in the general theoretical discussion.

A careful review of the apparatus showed that the only source of oxygen which could not be eliminated readily was in the fluorine. It was therefore decided to replace this cell with one which would produce as pure fluorine as possible.

Section IV

Introduction

The sensitivity of the reaction to oxygen and the critical effect of oxygen on the yield of S_2F_{10} indicated the necessity of obtaining a source of pure fluorine. This need was further demonstrated by the results of run 15A where 22.4 per cent S_2F_{10} was found. Although only an isolated experiment, this run showed the potentially large amounts of S_2F_{10} that could be produced with this system even in the absence of gaseous dilution.

During this time, the Electrochemistry Department at Toronto University had successfully constructed a low temperature generator which produced fluorine of approximately 95 per cent purity (9). This equipment was transferred to McGill and incorporated into the set-up by Dr. Burt-Gerrans and Mr. C.W. MacKinnon. With this new cell, it was hoped that large yields could now be obtained under commercial conditions. Since nitrogen dilution was not suitable for large scale production most of the trends were investigated in the absence of any gaseous diluent.

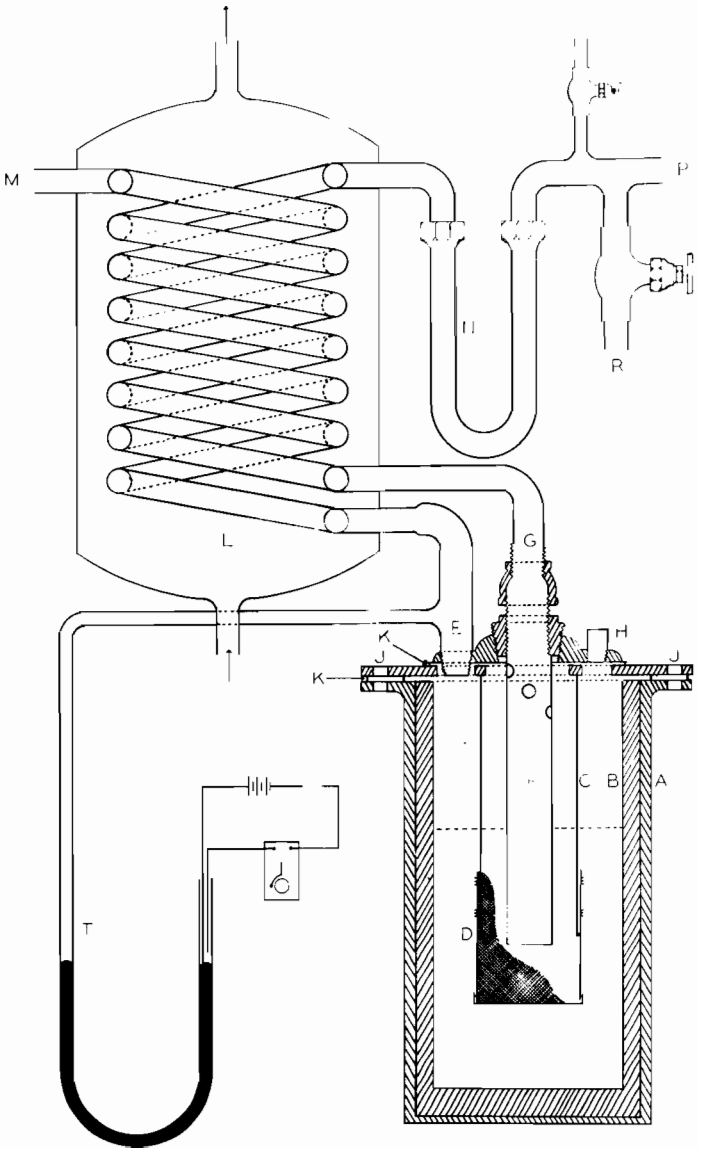
Apparatus and Techniques

The Second Fluorine Generator

The apparatus was essentially the same as that used in Section III with the exception of the new fluorine cell. This generator and its auxiliary parts are shown in Figure 13.

Figure 13

The Second Fluorine Generator


M
P
R
L
G
E
H
K
J
C
B
A
T
D

It consisted of a graphite pot (B), 5" in diameter, 9" long and 1/2" thickness, surrounded by a black iron cylinder (A) flanged at the top. The graphite and iron were machined to make a close fit and the former served as the anode. A sheet nickel diaphragm (C) was supported by a ring cover which was bolted to the pot flange at J. A gauze (D) was attached to the diaphragm as shown and consisted of a single layer of 35 mesh 0.010" monel wire, bound on with No. 24 nickel wire. This gauze supported a sheet nickel bottom.

The combined cathode (F) and hydrogen outlet (G) was supported by another iron ring which was bolted to the first. To provide an outlet for the hydrogen, the iron pipe cathode was vented at the top as shown. The rings were insulated from each other and from the pot by asbestos paper gaskets (K). Insulation for the bolts consisted of fibre bushings and washers. The first ring supported a thermometer well not shown in the figure. The second ring supported the fluorine outlet E and the plug H which could be removed for sampling of the electrolyte. An auxiliary line in G, not shown in the diagram, allowed for the addition of HF.

Electrical connection was made to the anode and cathode by copper strips welded to the iron flange and to the hydrogen outlet respectively. For cooling at the higher electrolysing currents, the pot was provided with a jacket through which oil could be circulated. This jacket was surrounded by a nichrome wire heater threaded vertically in

the channels of the inside layer of standard corrugated asbestos insulation. The bottom of the cell rested on 1/2" asbestos mill board.

The electrolyte, about 10 to 12 lbs. of KHF_2 was dried by radiant heat at 140°C before addition to the cell. The composition of the melt was maintained close to KF, 1.8 HF. This was accomplished by following the melting point and adding HF whenever the measurement indicated a low HF content. To obtain a melting point, H was removed and a copper-plated, copper - constantan thermocouple, fitted with a plug assembly for a four prong radio socket, was dipped into the electrolyte for a moment. It was quickly withdrawn and carried a drop of the electrolyte which was allowed to solidify. The thermocouple was then mounted in the plug so that electrical connection was made to a galvanometer. The assembly was gently heated by a Nichrome heater and the galvanometer reading taken when the electrolyte became molten and dropped off the thermocouple junction. The mole ratio was read directly from the galvanometer reading on a calibration chart prepared from Cady's data (5). The method had been checked by direct analysis of the melt composition and was accurate for mole ratios between 1.0 and 1.8 (9).

The anode compartment of the cell was provided with a mercury manometer T which was set to operate a warning bell when the differential pressure between the anode and the cathode chambers reached 5 mm. of mercury.

The fluorine and hydrogen passed from the generator through 1/2" stream line copper pipes into a water-cooled condenser L. A $CaCl_2$ drying tower to prevent the entrance of moist air was attached to the hydrogen outlet (M). Since the vapor pressure of HF was still high at the temperature of the condenser, a U-tube packed with dry NaF pellets was connected to the fluorine outlet. This removed all the HF from the fluorine stream. The condenser and the U-tube were connected to the line by unions which were readily removable and equipped with rubber washers. Replacement of the NaF was necessary approximately every 100 hours of operation. From P, the fluorine entered the apparatus shown in Figure 8, and the copper was connected with glass by de Khotinsky cement.

The outlets at S and R were employed for sampling and current efficiency determinations and were closed off by globe valves when not in use. A simple apparatus and technique was developed for the analysis of the fluorine stream. A glass sample tube of approximately 100 cc. volume, provided with stopcocks at both ends, was connected with S and the valve opened. The tube was flushed free of air and a sample taken by passing fluorine through for 10 to 15 minutes with the generator operating at approximately 10 amperes. The stopcocks were closed and the tube, whose volume had been measured accurately, was weighed. The stopcocks were handled so that the contents of the tube were at atmospheric pressure. Approximately 5 ml. of mercury was added and the tube and its

contents shaken until complete reaction had taken place. It was then weighed again and allowed to fill to atmospheric pressure with water. A final weighing was then made and simple calculation yielded the total volume of mercury and water which had replaced the fluorine. Knowing the volume of the bulb, the purity of the fluorine could then be found. All analyses with fluorine from the new generator showed more than 95 per cent purity. It should be mentioned that with this method any water soluble material would be absorbed and the values obtained would be high.

Current efficiencies were measured by drawing the fluorine from R through a concentrated solution of KI and titrating the liberated iodine. The gas was diluted with a large volume of air which entered at S. In this way, all the fluorine passed through the KI scrubber. The runs were usually done with the generator operating at 10 amperes for 10 minutes while the KI was vigorously stirred to ensure complete reaction. Current efficiencies were usually of the order of 90 per cent.

The Reactors

Although most of the experiments were done with the 1" reaction tube shown in Figure 4, some runs were later carried out in a 4" reactor. This tube was closed at one end with a copper plate which carried a 3/8" inlet. The other end was provided with a standard iron pipe cap which threaded on to the reactor and seated on a flange which had been

soldered to the outside of the reaction tube. An outlet tube of 3/8" copper pipe passed through the center of the cap and a rubber gasket provided an air-tight seal between the cap and the flange. The reactor was thermostated by soldering it into a container in which water could be maintained at any desired temperature.

Procedure

The only modifications in procedure were to ensure the absence of leaks and oxygen in the system. All seals before the reactor were made with de Khotinsky cement. If no nitrogen diluent was used, the rate of bubbler formation in the KI bubbler (J - Fig.8) decreased continuously as the nitrogen in the reactor was displaced by products. If the system was leak-proof this rate fell off to 1 to 3 cc./min. The absence of colour in the bubbler indicated that no fluorine was passing the reaction tube unchanged.

Results

The influence of six variables on the solid sulphur - fluorine reaction was investiaged.

1. Rate of fluorine flow
2. Amount of NaF diluent
3. Amount of gaseous diluent
4. Temperature
5. Copper diluent
6. Size of reaction tube

The data obtained are shown in Tables XI to XVIII at the end of this section and are represented graphically in Figures 14 to 18.

Although yields on both fluorine and sulphur have been calculated, and included in the tables, the fluorine trends have not been shown in some of the figures. It will be seen (**Tables XI** and XII) that the yields based on fluorine do not differ to any marked extent from those calculated on sulphur. They are included since fluorine costs are important from a production viewpoint. The discussion of results will be concerned with the yields on sulphur unless otherwise stated.

A complete analysis of the results is again postponed to the general discussion.

Effect of Fluorine Variation

The effect of the rate of fluorine flow is shown in Table XI and Figure 14. The yield of S_2F_{10} rose sharply as the rate of fluorine flow was decreased, and reached a maximum yield of 30.7 per cent at a fluorine rate of 7.5 cc./min. This change was accompanied by a decrease in the yield of SF_6. The inflection in the S_2F_{10} at 15 cc./min. of fluorine pointed to a limiting yield of approximately 31 per cent at very low fluorine rates.

Effect of NaF Diluent

The effect of diluting 10 gm. of sulphur with

varying amounts of NaF is shown in Table XII and Figure 15. Addition of NaF first resulted in a marked increase in S_2F_{10} but seemed to approach a limiting value. The trend was not followed any further since a physical limit on the amount of NaF which could be added was determined by the size of the reaction tube. Corresponding with this change in the amounts of S_2F_{10}, there was a continuous decrease in the yield of SF_6 and a slow increase in lower fluorides.

Effect of Nitrogen Dilution

Table XIII shows the effect of nitrogen dilution in the absence of any solid diluent at a fluorine rate of 90 cc./min. (solid line - Fig.11). The same trends were observed as in other gaseous diluent investigations (cf. Figs. 7 and 11), but the maximum yield of S_2F_{10} was slightly lower than that obtained when NaF was present.

The series of experiments shown in Table XIV and Figures 16 and 17 represent an attempt to increase the yield above 30 per cent, the maximum obtained at low fluorine rates. Nitrogen in varying amounts was added to 15 cc./min. of fluorine, and the temperature was varied at the high nitrogen flow rate. A sharp decrease in S_2F_{10} to 21 per cent was observed with increased gaseous diluent. On warming the reaction vessel, the yield rose again to 26 per cent.

Effect of Temperature

The temperature effects were investigated at fluorine

flow rates of 15, 30, 60 and 90 cc./min. (Table XV and Fig.18). The yields of lower fluorides decreased and those of SF_6 increased with a rise in the temperature which confirmed the trends suspected in Section I. The amounts of S_2F_{10} fell off above 35°C, and although only two values were determined at -40°C, the trends of Figure 18 indicated that the best yield at this temperature would be less than 30.7 per cent. At all temperatures, the yield of S_2F_{10} was higher at the lower fluorine rates. It is interesting to note the maximum yield at different temperatures

Temperature	Max. Yield of S2F10
0°C	30.7
45°C	25.0
85°C	22.5

Experiments with Copper Diluent

Experiments in Section I indicated that copper might serve as a better diluent than NaF. Tables XVI and XVII show some of the results obtained using copper powder under different conditions. Although yields as high as 28.6 per cent S_2F_{10} were obtained, further investigation was abandoned when the diluent was found to be a mixture of copper, copper sulphide, and copper fluoride, with the latter two increasing proportionally from run to run. This made it impossible to obtain a constant composition of the solid diluent and reproducible results. In addition no check on the sulphur balance was possible.

Effect of Size of Reaction Tube

To determine whether the results could be duplicated on a larger scale, a series of experiments was done in the 4" reactor (Table XVIII). An attempt was made to simulate the conditions for maximum yield in the small reactor. The flow rate of fluorine was 120 cc./min. and this space velocity would correspond to 7.5 cc./min. in the 1" reaction tube. The first set of runs was inconsistent and gave low yields of S_2F_{10}. Since the large reactor had been installed when the weather was very humid, and since Mungen and Lossing (12) had indicated that moisture had a deleterious effect on the production of S_2F_{10}, it was suspected that incomplete drying of the reaction system and reactants was responsible. After run 86B, precautions were taken to exclude moisture and the yields in the 4" reactor were comparable to those obtained in the small reactor, as shown below

Run No.	Size of Reactor in.	Fluorine cc./min.	Temp. °C	S/NaF Ratio	Size of Charge gm.	% Yield on Sulphur L.F.	SF_6	S_2F_{10}	SO_2F_2
16B	1	7.5	0	10/50	60	25.2	39.0	30.7	4.8
88B	4	120	0	10/50	1500	21.2	50.7	26.2	1.9

Mole Ratio of Fluorine to Sulphur

As mentioned previously, F/S ratios were determined in the caustic bubblers to obtain some insight into the composition of the lower fluorides. Although the values are included in the tables, it is evident that no trends are indicated and that no conclusions can be drawn from the results.

In addition to the inaccuracies in the analyses for fluoride ion at low concentrations (cf. Section II), slight reaction of the lower fluorides with the glass of the product trap and with the inlet tube of the first bubbler was observed. Since reaction with glass is known to produce oxyfluorides, and fluosilicates which may remain on the glass walls, it was evident that this would result in a further error in the F/S ratio.

The investigation of the oxygen effect indicated that the addition of oxygen resulted in larger amounts of lower fluorides, and it was suspected that the rapid increase was due to the increased production of the oxyfluoride SOF_2. This change would predominate in the lower fluorides and a trend in F/S towards the value of 2/1 should have been observed. However, as shown in Table X, the values were inconsistent and hence no trend was indicated.

Finally, the possible presence of compounds like SOF_2, SiF_4 etc. in the bubblers showed that the F/S ratio would be an average of many different types of molecules.

No confidence could therefore be placed in the ratio obtained, and the values have not been discussed in this thesis.

TABLE XI

Effect of Fluorine Variation

Weight sulphur in charge = 10 gm.
Nitrogen rate = 0 cc./min.
Reaction tube = 1 inch diameter
Temperature = 0°C

Run No.	Fluorine cc./min.	Wt. NaF gm.	Sulphur Reacted gm.	% Yield on Sulphur L.F.	SF_6	S_2F_{10}	SO_2F_2	Fluorine Reacted gm.	% Yield on Fluorine L.F.	SF_6	S_2F_{10}	SO_2F_2	F/S Ratio
16B	7.5	50	3.74	25.2	39.0	30.7	4.8	10.84	18.2	48.1	31.6	1.9	3.52
14B	15	50	2.89	26.6	40.0	29.3	4.6	8.13	16.9	50.4	30.9	2.0	3.00
4B	30	50	4.12	21.4	50.1	22.6	6.1	11.51	14.3	59.0	24.1	2.4	3.17
3B	45	50	4.04	19.3	56.2	17.2	7.3	11.91	11.7	68.1	17.4	2.9	3.01
7B	60	50	4.03	18.8	62.6	12.8	5.3	12.13	10.9	74.2	12.6	2.3	2.94
11B	60	50	4.31	19.4	58.5	16.3	5.8	13.11	11.4	68.5	15.9	4.2	3.01
12B	90	50	3.61	10.6	78.7	8.3	2.4	12.21	8.8	83.1	7.2	0.8	4.72
5B	135	50	2.96	16.0	78.3	2.8	2.8	9.78	11.8	84.6	2.6	1.1	4.10

TABLE XII

Effect of NaF Variation

Weight sulphur in charge = 10 gm.
Nitrogen rate = 0 cc./min.
Reaction tube = 1 inch diameter
Temperature = 0°C

Run No.	Fluorine cc./min.	Wt. NaF gm.	Sulphur Reacted gm.	% Yield on Sulphur L.F.	SF_6	S_2F_{10}	SO_2F_2	Fluorine Reacted gm.	% Yield on Fluorine L.F.	SF_6	S_2F_{10}	SO_2F_2	F/S Ratio
23B	90	0	3.62	6.6	90.4	1.5	1.4	12.35	3.9	94.3	1.4	0.5	3.38
21B	90	25	3.41	7.6	84.2	8.2	0.0	11.60	4.9	87.9	7.1	0.0	3.63
12B	90	50	3.61	10.6	78.7	8.3	2.4	12.21	8.8	83.1	7.2	0.8	4.72
22B	90	100	3.32	9.0	77.0	9.4	4.5	10.71	4.3	85.2	8.7	1.7	2.59
30B	90	100	3.63	10.4	77.3	10.5	1.9	12.35	5.6	84.6	9.2	0.1	3.07
25B	90	125	3.61	11.9	67.8	17.2	3.2	11.46	6.5	76.2	16.1	1.2	3.09
36B	90	125	4.11	11.7	68.3	17.4	2.6	13.12	6.6	76.1	16.2	1.0	3.04
40B	90	150	3.66	14.9	64.8	14.9	5.8	11.11	7.4	75.9	14.5	2.2	2.54
44B	90	240	3.75	17.1	62.2	15.7	5.0	11.31	9.3	73.3	15.5	1.9	2.77

TABLE XIII

Effect of Nitrogen Dilution in Series B

Weight sulphur in charge = 10 gm.
Weight of solid diluent = 0 gm.
Reaction tube = 1 inch diameter
Fluorine rate = 90 cc./min.

Run No.	Nitrogen cc./min.	Temp. °C	Sulphur Reacted gm.	% Yield on Sulphur L.F.	SF_6	S_2F_{10}	SO_2F_2	Fluorine Reacted gm.	% Yield on Fluorine L.F.	SF_6	S_2F_{10}	SO_2F_2	F/S Ratio
23B	0	0	3.62	6.6	90.4	1.5	1.4	12.35	3.9	94.3	1.4	0.5	3.38
53B	300	0	4.01	22.4	67.5	10.2	0.0	12.18	10.7	79.5	10.0	0.0	2.45
56B	500	0	3.89	36.4	50.5	11.8	1.3	11.00	23.4	63.5	12.4	0.3	3.06
65B	600	0	4.15	37.4	48.3	13.4	1.0	11.75	24.8	60.5	14.1	0.4	3.17
57B	700	0	4.06	50.4	26.1	23.0	0.6	11.70	35.4	40.7	23.6	0.3	3.41
59B	900	0	4.37	64.4	16.6	18.4	0.8	10.54	52.5	24.4	22.6	0.4	3.32

TABLE XIV

Effect of Nitrogen and Temperature at a Low Fluorine Rate

Weight sulphur in charge = 10 gm.
Weight of NaF diluent = 50 gm.
Reaction tube = 1 inch diameter
Fluorine rate = 15 cc./min.

Run No.	Nitrogen cc./min.	Temp. °C	Sulphur Reacted gm.	% Yield on Sulphur L.F.	SF_6	S_2F_{10}	SO_2F_2	Fluorine Reacted gm.	% Yield on Fluorine L.F.	SF_6	S_2F_{10}	SO_2F_2	F/S Ratio
14B	0	0	2.89	26.6	40.0	29.3	4.6	8.13	16.9	50.4	30.9	2.0	3.00
31B	25	0	3.86	46.8	24.4	28.1	0.7	10.35	35.8	32.4	31.2	0.3	3.46
28B	100	0	3.77	70.1	7.1	20.8	1.4	7.81	56.3	13.2	29.8	0.8	3.13
51B	100	45	3.54	46.5	25.9	26.1	1.3	8.26	26.4	39.6	33.3	0.7	2.22
52B	100	85	3.34	32.4	41.0	25.1	1.6	8.73	16.8	54.2	28.5	0.7	2.28

TABLE XV

Effect of Temperature Variation

Weight sulphur in charge = 10 gm.
Weight of NaF diluent = 50 gm.
Nitrogen rate = 0 cc./min.
Reaction tube = 1 inch diameter

Run No.	Fluorine cc./min.	Temp. °C	Sulphur Reacted gm.	% Yield on Sulphur L.F.	SF_6	S_2F_{10}	SO_2F_2	Fluorine Reacted gm.	% Yield on Fluorine L.F.	SF_6	S_2F_{10}	SO_2F_2	F/S Ratio
61B	15	-40	2.54	64.3	9.6	18.7	7.5	5.93	57.9	14.7	23.7	3.8	3.55
14B	15	0	2.87	26.6	40.0	29.3	4.6	8.13	16.9	50.4	30.9	2.0	3.00
54B	15	45	2.76	8.9	62.8	25.8	4.6	8.61	4.0	71.6	22.6	1.7	2.35
58B	15	45	2.38	8.9	62.4	24.5	4.2	7.48	4.6	70.7	23.2	1.5	2.74
55B	15	85	2.75	5.1	68.6	21.9	4.4	8.82	1.9	76.2	20.3	1.6	2.04
62B	30	-40	3.44	33.8	47.9	15.0	3.5	9.99	24.6	58.7	15.3	1.4	3.58
66B	30	-40	3.63	33.9	40.7	19.4	6.1	10.15	25.0	51.8	20.6	2.6	3.48
4B	30	0	4.12	21.4	50.1	22.6	6.1	11.51	14.3	59.0	24.0	2.4	3.17
47B	30	45	3.79	9.8	64.7	23.9	1.6	11.79	2.6	74.0	22.8	0.6	1.39
49B	30	90	3.75	7.3	70.1	19.3	3.1	11.85	1.5	79.1	18.2	1.2	1.11
7B	60	0	4.03	18.8	62.6	12.8	5.9	12.13	10.9	74.2	12.6	2.3	2.94
11B	60	0	4.31	19.4	58.5	16.3	5.8	13.11	11.4	68.5	15.9	4.2	3.01
45B	60	45	3.05	10.4	68.2	14.8	6.5	9.35	4.2	80.1	13.3	2.5	2.06
46B	60	85	3.45	5.6	84.1	8.0	2.2						
12B	90	0	3.61	10.6	78.7	8.3	2.4	12.21	8.8	83.1	7.2	0.8	4.72
48B	90	45	3.48	8.4	82.3	5.5	3.9	11.17	2.5	90.8	5.1	1.4	1.59
50B	90	80	3.56	8.0	86.9	2.0	3.4	11.58	1.9	95.2	1.8	1.2	1.32

TABLE XVI

Effect of Copper Variation

Weight sulphur in charge = 10 gm.
Nitrogen rate = 0 cc./min.
Reaction tube = 1 inch diameter
Temperature = 0°C

Run No.	Fluorine cc./min.	Wt. Cu gm.	Sulphur Reacted gm.	% Yield on Sulphur L.F.	SF_6	S_2F_{10}	SO_2F_2	Fluorine Reacted gm.	% Yield on Fluorine L.F.	SF_6	S_2F_{10}	SO_2F_2	F/S Ratio
23B	90	0	3.62	6.6	90.4	1.5	1.4	12.35	3.9	94.3	1.4	0.5	3.38
26B	90	25	3.83	8.7	68.2	20.2	3.1	12.30	4.6	75.6	18.7	1.1	2.84
27B	90	50	3.49	18.3	60.2	17.2	4.2	10.48	9.7	71.6	17.1	1.7	2.67
34B	90	100	3.76	17.1	61.4	17.7	3.9	11.45	9.5	71.7	17.3	1.5	2.86
24B	90	200	3.53	57.0	33.6	5.6	3.9	7.91	37.0	53.5	7.5	2.0	2.45

TABLE XVII

Effect of Fluorine Variation in the Presence of Copper Diluent

Weight sulphur in charge = 10 gm.
Nitrogen rate = 0 cc./min.
Reaction tube = 1 inch diameter
Temperature = 0°C

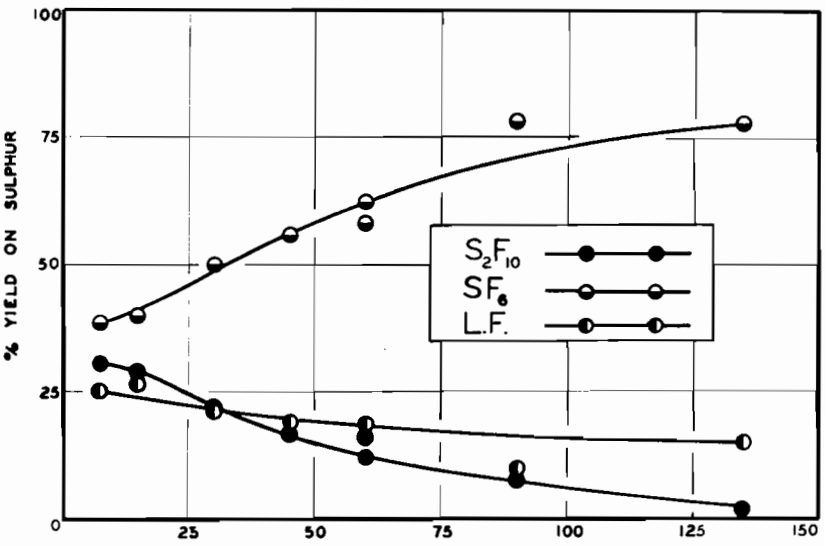
Run No.	Fluorine cc./min.	Wt. Cu gm.	Sulphur Reacted gm.	% Yield on Sulphur L.F.	SF_6	S_2F_{10}	SO_2F_2	Fluorine Reacted gm.	% Yield on Fluorine L.F.	SF_6	S_2F_{10}	SO_2F_2	F/S Ratio
33B	15	25	3.23	26.1	46.0	24.2	3.6	9.57	19.1	55.2	24.2	1.5	3.67
35B	30	25	4.12	19.1	49.7	28.6	2.8	12.96	12.2	59.7	26.9	1.1	3.40
32B	60	25	3.95	15.4	63.2	19.2	2.3	12.52	10.3	70.8	17.9	0.9	3.57
26B	90	25	3.83	8.7	68.2	20.2	3.1	12.30	4.6	75.6	18.7	1.1	2.84

TABLE XVIII

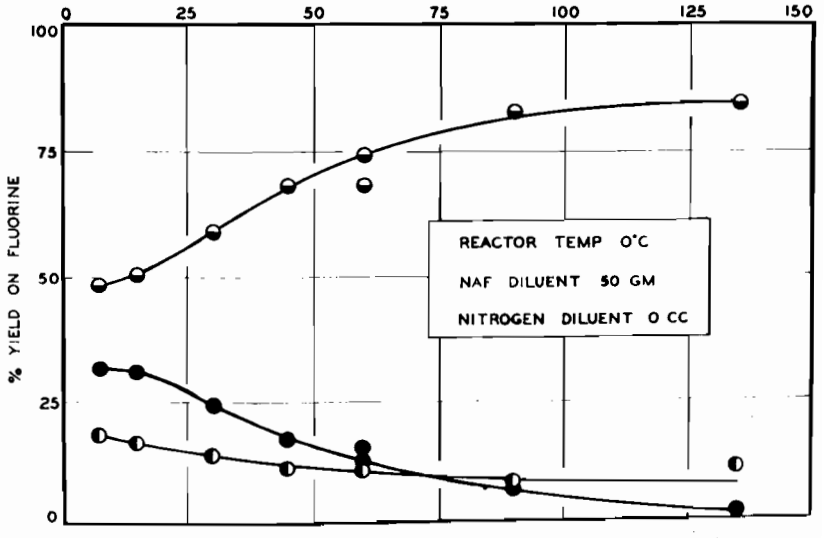
Experiments with Large Reaction Tube

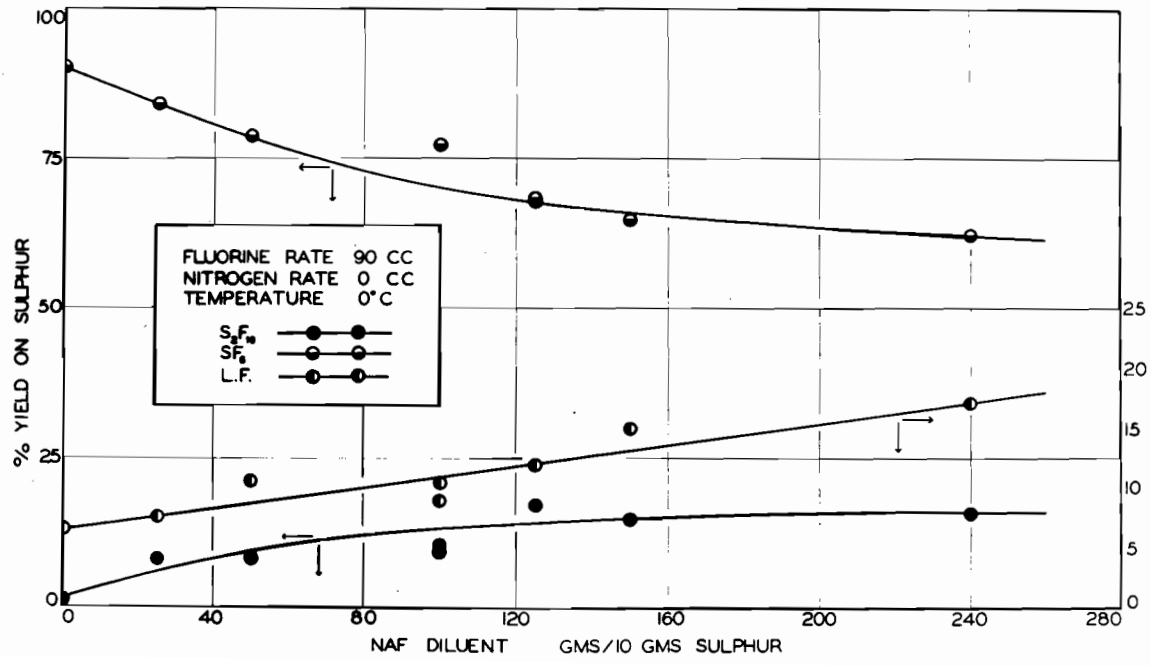
Reaction tube = 4 inch diameter
Nitrogen rate = 0 cc./min.
Temperature = 0°C

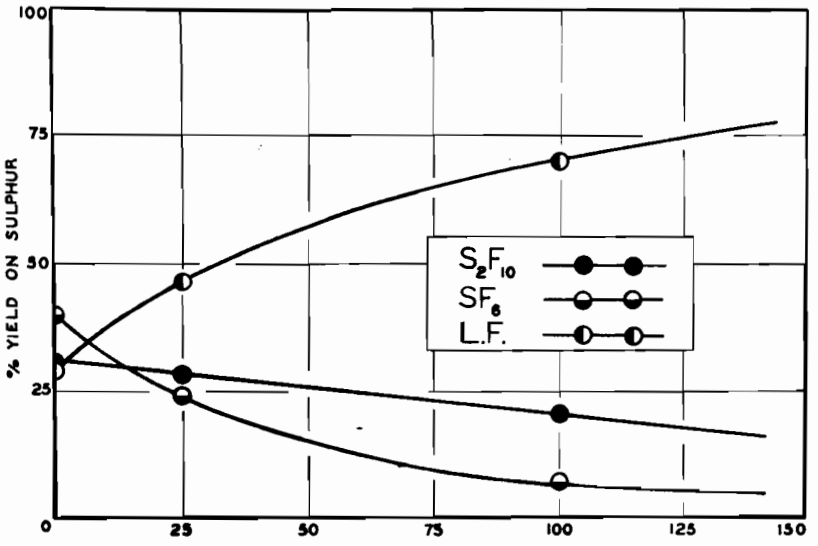
Run No.	Fluorine cc./min.	S/NaF	Sulphur Reacted gm.	% Yield on Sulphur L.F.	SF_6	S_2F_{10}	SO_2F_2	Fluorine Reacted gm.	% Yield on Fluorine L.F.	SF_6	S_2F_{10}	SO_2F_2	F/S Ratio
73B	150	10/0	4.59	32.2	49.1	10.7	8.0	12.91	23.2	62.1	11.3	3.3	3.40
78B	30	10/50	3.48	53.2	30.5	12.8	3.5	8.35	37.2	45.7	15.9	1.7	2.82
79B	120	10/50	4.81	41.3	39.6	12.9	6.0	12.73	29.3	53.4	14.5	2.7	3.15
70B	150	10/100	4.71	36.0	41.9	16.6	5.5	12.85	24.9	54.5	18.1	2.4	3.18
76B	150	10/100	4.27	30.7	47.8	20.5	1.1	12.38	19.8	58.7	20.5	0.5	3.76
69B	150	10/200	4.17	22.6	45.1	17.7	14.7	11.05	13.1	60.4	19.8	6.6	2.60
68B	150	10/300	3.67	39.2	33.3	17.4	10.2	12.83	21.8	59.8	14.8	3.5	3.28
75B	150	10/300	4.06	39.0	38.9	17.8	4.2	10.89	27.0	51.7	19.7	1.9	3.12
74B	150	10/500	4.30	31.1	48.8	16.5	3.7	12.21	21.2	61.1	17.2	1.5	3.10
77B	30	10/500	4.37	52.5	30.4	12.4	4.7	9.92	33.8	47.6	16.3	2.5	2.46
85B	120	1000/0	3.45	72.3	18.9	2.6	6.2	10.23	72.3	22.5	2.7	2.5	2.77
81B	120	300/1500	5.24	46.8	41.3	9.6	2.3	15.33	29.6	57.9	11.2	1.1	2.72
86B	120	1000/0	4.09	37.8	44.3	11.9	6.0	10.99	25.5	58.7	13.2	2.6	3.06
87B	120	1000/0	4.39	34.4	47.0	13.6	5.1	12.29	23.8	59.6	14.4	2.2	3.26
89B	120	500/1300	4.87	43.3	37.5	10.9	8.2	12.28	30.2	53.1	12.9	3.9	2.70
88B	120	300/1500	4.35	21.2	50.7	26.2	1.9	13.20	13.7	59.8	25.6	0.8	3.31
90B	120	210/1590	4.50	38.4	40.6	14.5	6.3	12.71	30.6	51.2	15.3	2.7	3.80
94B	120	90/1710	6.07	8.7	62.6	26.8	1.9	19.55	5.3	69.2	24.8	0.7	3.35



FLUORINE RATE CC/MIN




FLUORINE RATE 90 CC
NITROGEN RATE 0 CC
TEMPERATURE 0°C
S_2F_{10}
SF_6
L.F.
% YIELD ON SULPHUR
NAF DILUENT GMS/10 GMS SULPHUR
0
25
50
75
100
0
40
80
120
160
200
240
280
5
10
15
20



NITROGEN RATE CC/MIN

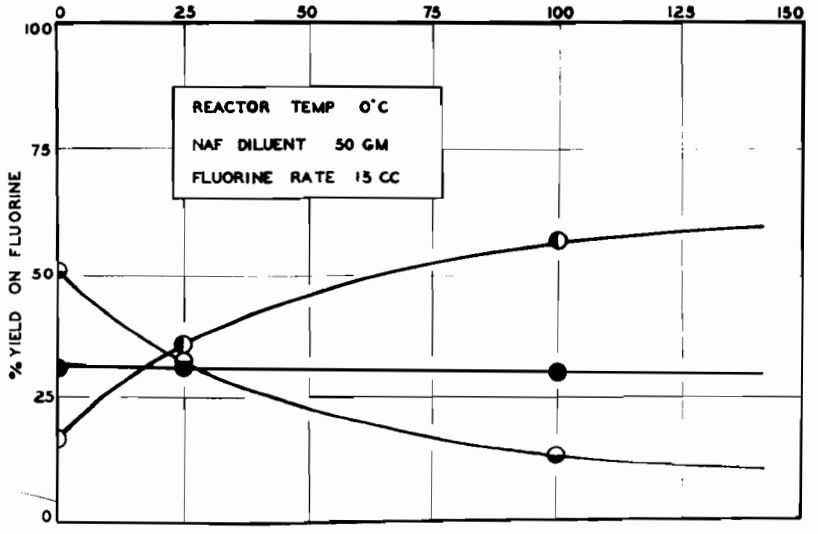
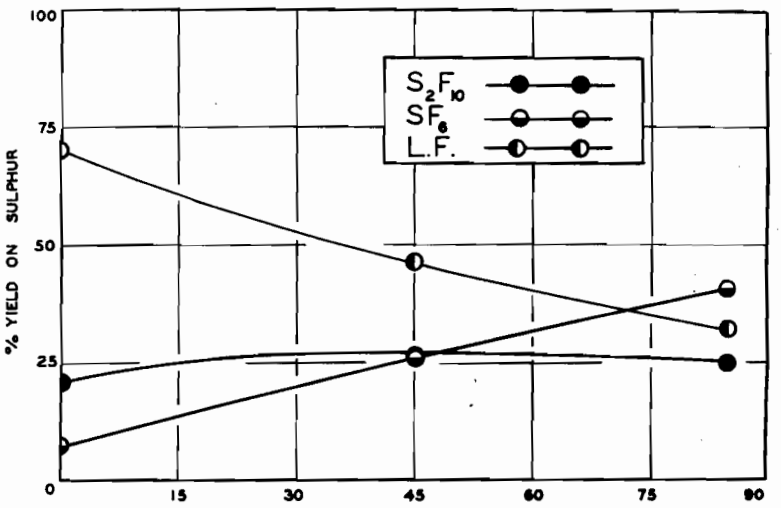
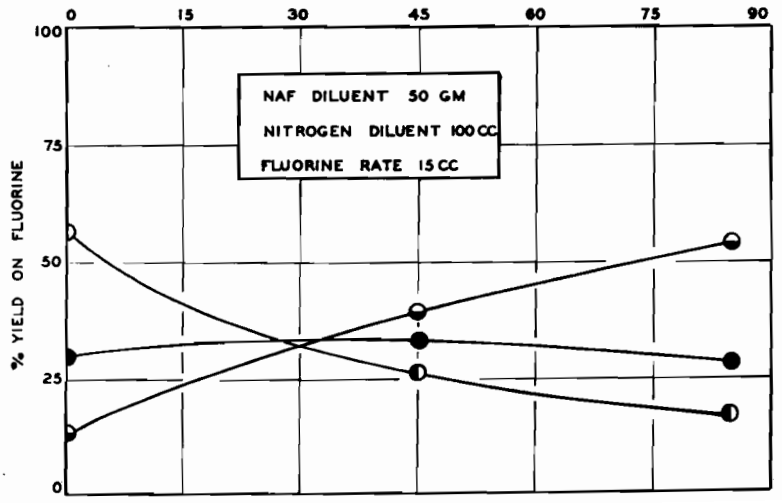
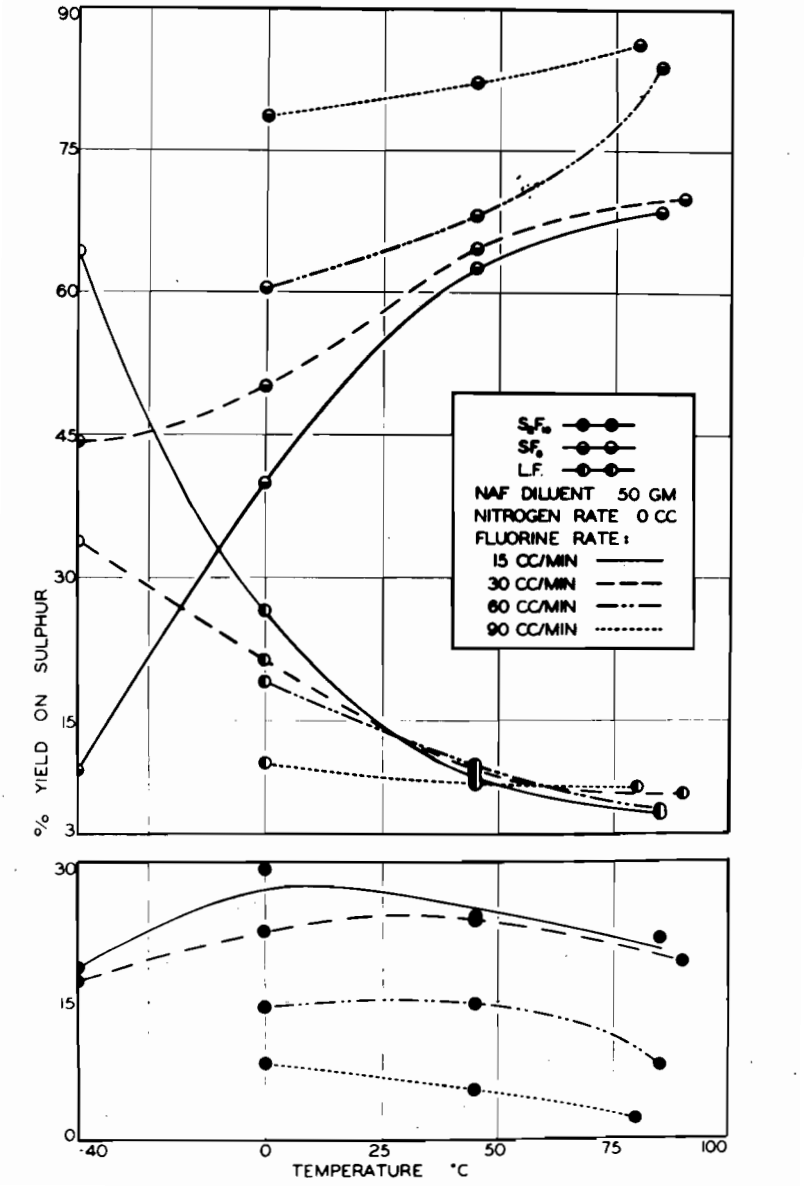


Figure 17

The Effect of Temperature in the Presence of Nitrogen at a Low Fluorine Rate


100
75
50
25
0
% YIELD ON SULPHUR
S_2F_{10}
SF_6
L.F.
15
30
45
60
75
90
TEMPERATURE °C


0
15
30
45
60
75
90
100
75
50
25
0
% YIELD ON FLUORINE
NAF DILUENT 50 GM
NITROGEN DILUENT 100 CC
FLUORINE RATE 15 CC


90
75
60
45
30
15
3
% YIELD ON SULPHUR
S_2F_2
SF_2
L.F.
NAF DILUENT 50 GM
NITROGEN RATE 0 CC
FLUORINE RATE:
15 CC/MIN
30 CC/MIN
60 CC/MIN
90 CC/MIN
30
15
0
-40
0
25
50
75
100
TEMPERATURE °C

DISCUSSION

Throughout the course of this work, it has been evident that the mechanism of the reaction of fluorine and sulphur could not be elucidated by the ordinary kinetic methods. The situation was complicated by the essentially dynamic nature of the system, the variety and number of products, and the difficulties attendant upon the isolation and identification of the lower fluorides.

However, temperature control at the point of reaction has been shown to be the most important factor in determining the yields of the various products.

With this in mind, and from the general facts arising out of the experimental work in Section IV, an hypothesis has been developed which furnishes a reasonable explanation for the trends which have been observed with the many variables. Although it is not claimed that this hypothesis is the only one which can be shown to fit the experimental data, it is believed that any other theory would necessitate more assumptions than will be needed here.

As mentioned before, the reaction between fluorine and sulphur is extremely energetic and exothermic. Although it is known that the heat developed when pure sulphur is used is enough to melt the solid, there is no evidence that such a physical change occurs when the reaction is carried out under controlled conditions. In the discussion which follows, the reaction is therefore assumed to take place on the surface of

a solid rhombic sulphur crystal.

Mark and Wigner have shown that such a crystal consists of an interlocked lattice of sulphur atoms in which a space cell contains 128 units (40). Each crystal would present for reaction a surface of sulphur atoms linked to each other and to other units in the body of the solid.

The reaction may therefore be assumed to occur in the following manner. Fluorine molecules or atoms will collide with the surface lattice of atoms, adsorb momentarily and react. The energy released by this reaction will result in the rupture of various S - S bonds and the formation of numerous sulphur - fluorine fragments which will immediately be vaporized from the crystal.

The nature of the fragments, which could contain 1,2,3--- atoms of sulphur, has not been ascertained. However, there is very little evidence for the existence of groups containing more than two sulphur atoms. Although it has not yet been possible to isolate any of the intermediates in the products of the sulphur - fluorine reaction, the behaviour of the lower fluorides would indicate that these compounds, at least, consist of gases such as SF_4, S_2F_2, SOF_2 etc. Further, no fluorinated compounds which contain an S_3, S_4--- have been identified in this work or reported in the literature. The nature of the sulphur molecule itself is of interest in this regard. The existence of S_8, S_2, and S_1 groups has been established with certainty, but although some workers have

claimed that intermediates, such as S_4 and S_6, can be formed, they have never been able to isolate or identify these structures.

It would appear, then, that whereas the S_1 and S_2 fragments possess some inherent stability, the large fragments even if formed by the original reaction, would be unstable and would decompose.

Although it has been assumed, for convenience, that the sulphur acts as a rhombic crystal, it should be mentioned that the argument presented above is not radically changed if the sulphur melts before reaction. Although a lattice of atoms is no longer presented to the fluorine for reaction, there are still S_8 molecules in the liquid which can combine with the fluorine to yield similar fragments. However the probability of formation of S_3, S_4 etc. fragments will be further diminished because of the shorter sulphur chain length.

It is assumed in the following discussion that only S_1 and S_2 groups are formed. If an S_2 fragment is produced, the reaction will proceed in the following manner. Assuming that the S - S bond remains unbroken the fragment can be progressively fluorinated to S_2F_{10}. Pauling has given the bond energies for F - F and S - S as 63.5 and 65.8 kcals. respectively (41). At first glance, it might appear, then, that the energy released by the formation of the S - F linkages, whatever value they may have, would accumulate in the molecule and at some stage in the fluorination, result in the split of the S - S bond. However, during the many collisions necessary

for complete fluorination to S_2F_{10}, it is probable that this excess energy would be dissipated in further collisions either with the solid diluent, the walls, nitrogen diluent molecules, etc.

SF_6 will be formed from the complete fluorination of S_1 groups produced in the initial sulphur degradation. If, at any stage in the formation of S_2F_{10}, enough energy is available to split the S - S bond, two single sulphur fragments will result which may or may not be fluorinated to SF_6, but not to S_2F_{10}. Some workers have suggested that S_2F_{10} may be formed by fluorination and recombination of these S_1 "radicals". Although improbable, this type of mechanism is discussed in greater detail later.

Some energy (activation energy) will be needed to prepare both SF_6 and S_2F_{10} from the original fragments and experimental evidence indicates that the necessary energy will be greater for SF_6 than for S_2F_{10}. It has been found, for instance, that production of SF_6 is much more sensitive than S_2F_{10} to temperature changes.

However, it will be shown later that where there is reason to believe that the energy available for the activation of the fragments is comparatively low, the rate of formation of S_2F_{10}, as well as of SF_6, is affected markedly by temperature changes.

If the energy required for complete fluorination is not available, then the fragments will appear as lower fluorides.

During the nitrogen dilution experiments in Section I, a sulphur ring was often observed in the first liquid air product traps (cf. page 40). Since S_2F_2 is known to decompose on glass yielding sulphur, this indicates that possibly S_2F_2 was a fragment which was proceeding to S_2F_{10} but lacked the requisite energy for complete fluorination.

If it is assumed that the formation of S_2F_{10} is contingent on the presence of an S_2 linkage, it is obvious that the yield of S_2F_{10} will be related to the number of initial S_2 fragments produced. This number will, in turn, depend on the degree of degradation of the sulphur crystal. It does not seem improbable that the microscopic temperature at the point of reaction will determine the nature of this decomposition, and that the less the heat, the larger number of S_2 groups which will be formed. Since this temperature will be proportional to the rate of reaction, it is obvious that suitable variation of the reaction conditions will control the degree of degradation of the sulphur crystal and therefore the number of S_2 groups. The number of these groups will also depend on the temperature of the reaction vessel since it will contribute to the thermal energy at the point of reaction. The yields of S_2F_{10} and SF_6 will therefore be related both to the rate of reaction and the gross temperature of the reaction tube.

However, these yields will also be determined by the energy available in the gas phase for activation of the fragments. It is probable that this energy will be only slightly

affected by the rate of reaction since changes in the temperature of the solid bed should result in only slight variations in energy in the gas phase. In this connection, the effects of the temperature of the reaction vessel and the addition of gaseous diluent will be much more significant.

With these considerations in mind, a review will now be made of all the results obtained in this work and it will be shown that the trends are consistent with the general hypothesis that has been advanced.

During all the experiments in which sulphur was diluted with NaF a gradient of sulphur was observed in the bed. At the fluorine inlet, the sulphur had reacted through the entire depth of the NaF diluent. A little further along the tube only part of the NaF was depleted of sulphur, at the top of the bed, and this trend continued until the concentration of sulphur was uniform throughout the solid diluent. This indicated that the fluorine reacted over a measurable length of charge and was therefore always in contact with the products of reaction. Since the gradient was observed at all fluorine flows it can, therefore, be assumed that even at low rates enough fluorine was present to fluorinate the fragments completely if sufficient energy was available.

This was further confirmed when nitrogen was used to dilute the fluorine stream. When these dilutions were large, some fluorine passed through the reaction tube unchanged and was observed in the KI bubbler.

The effect of variation in fluorine flow is best examined by following the trends with decreasing rate (Table XI and Fig.14). As the rate of fluorine flow is diminished, the rate of reaction and, therefore, the microscopic temperature at the point of reaction will be decreased. This will result in a greater proportion of S_2's and an increase in S_2F_{10} as shown. Simultaneously, the yield of SF_6 will decrease since the number of S_1's will be diminished. As mentioned before, the decrease in the gross temperature of the solid bed will not significantly affect the thermal energy available in the gas phase. Since this is determined primarily by the temperature of the reaction vessel, sufficient energy will usually be present to allow the fluorination of S_1 and S_2 fragments to proceed almost to completion. However the thermal energy available for activation will be decreased slightly and consequently a small gradual increase in lower fluorides, at the expense of both S_2F_{10} and SF_6, is observed as the rate of fluorine flow is diminished.

At low fluorine rates (7.5 to 15 cc./min.) the yield of S_2F_{10} seems to be approaching a limiting value. This value will be determined by two factors. It is assumed that there is a limiting number of S_2 groups that can be formed and, therefore, the relation between this number and the degradation of the sulphur crystal will not be linear. It is probable, then, that the number of S_2 groups and therefore the S_2/S_1 ratio will not increase as rapidly in this region.

In addition, the thermal energy necessary to maintain the rate of fluorination may also be approaching a limiting value, so that even if S_2 fragments are formed, insufficient activation energy is present for reaction of these groups. This decrease in available energy will, no doubt, reduce the rate of formation of SF_6, so that its yield will also be affected easily at this point. Although no measurements were made at very low fluorine rates (less than 7.5 cc./min.), the yields of SF_6 and S_2F_{10} would probably decrease and the lower fluorides would increase.

From the above discussion, it is evident that at high fluorine rates enough energy is available in the gas phase to fluorinate nearly all the sulphur fragments. However, the rate of reaction and, therefore, the temperature of the solid bed is too high to yield enough S_2's to give large amounts of S_2F_{10}. If nitrogen is added to this system, the yield will be affected in two ways. The dilution of the fluorine stream will result in a decrease in the rate of reaction and therefore the sulphur crystal will be degraded in such a manner as to give more S_2 groups.

However, at the same time, by collision with the fragments, nitrogen will also be effective in removing energy necessary for fluorination.

These two factors, then, will counteract each other in determining the yield of S_2F_{10}. This is immediately apparent in Figures 7 and 11 (Tables IV, IX and XIII). Since the trends

obtained in all three series illustrate the same general characteristics, for convenience, the discussion will be concerned with the Series A runs (dotted line - Fig.11).

Up to 800 cc./min., although the energy available for activation is decreasing, enough S_2's are being formed to more than counteract this reduction and the yield of S_2F_{10} increases. However, beyond this point, the S_2 formation approaches its limiting value, the available energy still decreases, and the trends reverse with consequent decline in the yield of S_2F_{10}.

The two factors discussed above will also determine the trend in the amounts of SF_6. With increasing nitrogen dilution, the SF_6 yield will fall off due to both a decrease in the number of S_1's and a decrease in the rate of formation of SF_6 because of insufficient energy. The sharp gradient in the curve, and the low yields at high dilutions, indicate the importance of energy considerations in the production of SF_6.

Although nitrogen dilution should ultimately yield the same number of S_2 groups as that obtained at low fluorine rates, the yields of S_2F_{10} will, of course, be lower in the presence of a gaseous diluent. However, it is interesting to note that even at 800 cc./min. of nitrogen, enough energy is available to produce yields of S_2F_{10} only a few per cent less than the maximum yield at the low fluorine rates. This indicates that the activation energy necessary for the

fluorination of S_2 fragments to S_2F_{10} is not as large as that required for SF_6 and is probably very low.

This is further emphasized by comparison again with the fluorine curve. Corresponding to a 50 per cent yield of S_2F_{10} in the fluorine curve, the yield of SF_6 is approximately 40 per cent. In the presence of nitrogen, the yield of SF_6 is only about 10 per cent at the maximum S_2F_{10} value. This difference must be due to a thermal effect since the ratio of S_2/S_1 fragments is probably nearly the same at these points.

It might be suggested that the decreased yield of SF_6 and the limiting yields of S_2F_{10} in the presence of nitrogen are due to a reduction in the number of collisions between fluorine and the fragments. It might also appear that although the Mass Law is not directly applicable to this dynamic system, concentration factors would influence the yields of the various products. Thus, with increasing dilution of the fluorine stream, the rate of formation of SF_6 might be expected to follow the sixth power of the fluorine concentration, whereas the yield of lower fluorides would follow the third or fourth power of the fluorine concentration. Evidence will, however, be presented later to show that these considerations are of relatively minor importance and the yields of the different products are much more dependent on energy considerations.

Concomitant with the changes in SF_6 and S_2F_{10}, the yields of lower fluorides will increase rapidly. The sharp initial slope of the lower fluoride curve indicates again

that the energy considerations operate even at the low nitrogen flow rate.

The effect of nitrogen dilution in the absence of any solid diluent is also shown in Figure 11 (solid lines). Although in nearly all particulars, this curve is similar to the one just described, one point of interest should be noted. If fluorine is allowed to react with pure sulphur, the temperatures developed at the point of reaction will be much higher and therefore the number of S_2's will tend to be less. The addition of nitrogen with its consequent decrease in reaction rate will be of far greater importance in this system and the yield of S_2F_{10} will have a lower initial value but will increase much more rapidly. This accounts for the sharp gradient in the S_2F_{10} curve (shown in Fig.11 - solid line) up to 800 cc./min.

Figures 16 and 17 and Table XIV are interesting in this connection. It has been shown that at 15 cc./min. of fluorine, the number of S_2's is approaching a limiting value and the thermal energy available is just enough for fluorination of most of the fragments of S_2F_{10}. The addition of nitrogen at this point would, therefore, result in very little increase in S_2's, but would affect the energy relations in a profound manner. This latter effect will more than compensate for any possible increase in the number of S_2's. Consequently, the yield of S_2F_{10} decreases markedly in the presence of 100 cc./min. nitrogen.

As mentioned before, the decrease in available energy

will hinder the formation of SF_6 even more noticeably than S_2F_{10} as it requires a higher activation energy. In addition, since the number of S_1's will probably decrease, the yields of SF_6 fall off very rapidly. A simultaneous increase is observed in the amounts of lower fluorides.

Comparison of this curve with the Series A nitrogen curve (Figure 11) shows immediately that the nitrogen effect is much more significant at the low fluorine rate. Addition of 100 cc./min. nitrogen at 90 cc./min. fluorine causes only a 25 per cent decrease in SF_6, whereas the same volume of nitrogen at 15 cc./min. of fluorine results in a decrease of 75 per cent of the original value. In fact, at 90 cc./min. of fluorine, at least 900 cc./min. of nitrogen is necessary to obtain the same yield of lower fluorides (ca. 70 per cent) as that found when 100 cc./min. of nitrogen is added to the system at 15 cc./min. of fluorine.

This again emphasizes the critical low energy conditions in the vapor phase at the low fluorine rates. However, if the tube is heated (Fig.17 and Table XIV), enough heat should be provided to increase the rate of fluorination of S_2 and S_1 fragments and the yields of SF_6 and S_2F_{10} should increase.

The effect of this thermal energy on S_2F_{10} will be offset to some extent by the decrease in the number of S_2's with increasing temperature and the yield is therefore not restored to its original value of 50 per cent. The amount of

this decrease is indicated in Figure 18 where an increase of 45°C at 15 cc./min. fluorine in the absence of nitrogen results in a change in the yield of S_2F_{10} from 29 to 24 per cent.

It is interesting to note the complete reversal in the yields of SF_6 and lower fluorides in the presence of 100 cc./min. of nitrogen at 90°C. The initial addition of nitrogen decreases the yields of SF_6 and increases the yields of lower fluorides. Raising the temperature to 90°C reverses these trends and the resulting amounts of the products are almost identical with the original yields at 0 nitrogen dilution and 0°C. This indicates clearly that the major factor controlling the fluorination of lower fluorides is the macroscopic temperature in the gas phase and not the concentration or the number of collisions.

The effect of diluting the sulphur with a solid diluent is shown in Figure 15 and Table XII. The addition of NaF will first result in a decrease in the concentration of sulphur at any point and consequently the temperature developed will be lower. Since this temperature decrease in the solid bed determined the trends in the fluorine curve, it would be predicted that the NaF curve would show the same general features found in that curve. Initially, as expected, the trends are very similar. The yield of SF_6 decreases and that of S_2F_{10} increases rapidly and there is a slow change in lower fluorides.

However, if it is assumed that the primary function

of the NaF is to decrease the heat developed at any point in the bed, a limiting concentration will be reached beyond which the addition of the inert solid will be much less effective. Since NaF is a poor heat conductor, a sulphur crystal surrounded with excessive NaF will not decrease the temperature developed at that crystal markedly. Consequently the yields will change much more slowly beyond 50 to 75 gm. NaF.

It should be mentioned that the series was done at 90 cc./min. of fluorine so that the heat developed initially without any diluent was comparatively high.

Since copper would dissipate heat from the point of reaction much more efficiently than NaF, it might be expected that if sulphur was diluted with copper a higher yield of S_2F_{10} could be obtained at comparable fluorine flows. Comparison of Tables XI and XVII does indicate this relationship, the yields with copper being generally higher at all fluorine rates.

Simons has suggested that the production of S_2F_{10} and SF_6 follows a chain reaction mechanism and that NaF serves as a chain breaker. This reasoning can be applied to the considerations developed above. The addition of NaF would first lead to an increase in the number of S_2's as before. Simultaneously, the number of contact surfaces for the breaking of chains would be increased. These factors would counteract each other, the cooling effect being more important initially but becoming less so as NaF is added.

Although this may explain the trends in the S_2F_{10}

curve, many other questions are left unanswered. If the NaF breaks chains, it would be expected that the SF_6 would decrease at a constant rate and fairly rapidly. Since the breaking of chains would lead to incomplete fluorination, it would also be predicted that large NaF dilutions would give high yields of lower fluorides. As can be seen from the curve, these effects are not observed and it is therefore probable that chain breaking by NaF is unimportant.

In the early part of the S_2F_{10} investigations it had also been suggested that the solid diluents acted as catalytic agents, since the diluents found effective by Schneider all had similar ionic lattices. As pointed out in Section I, the high yields with copper, with a very different crystal structure, indicated that such an hypothesis was not plausible. Some of these copper experiments were repeated in Section IV (Tables XVI and XVII) and verified the earlier findings.

The work with the sulphur smoke (Section II) showed that yields of S_2F_{10} up to at least 10 per cent on sulphur could be produced without any solid diluent at all. This was further substantiated when the effect of nitrogen dilution in the presence of pure sulphur was studied (Table XIII and Fig.11). Yields of S_2F_{10} could be produced that were nearly as high as those obtained in the presence of solid diluent.

It was shown conclusively, therefore, that NaF did not catalyse the reaction to S_2F_{10}, and probably acted as a heat dissipator.

Throughout this work it has become increasingly evident that the yields of the various products are determined by the temperature in either the solid bed or the vapor phase. The temperature of the reaction tube was therefore varied to find to what extent these effects were governed by macroscopic temperature changes (Fig.18 and Table XV).

In the light of the hypothesis developed above, an increase in the temperature of the reaction vessel would have a twofold effect. The increased temperature of the solid bed would lead to a decrease in the number of S_2's and the increased thermal energy in the gaseous phase would increase the rate of fluorination of fragments to SF_6 and S_2F_{10}.

It has been shown that at a fluorine rate of 15 cc./min., although the number of S_2's has not yet reached its limiting value, the available energy may not be high enough to permit fluorination of all of the S_2's to S_2F_{10}. A decrease in temperature below 0°C might yield more S_2's, but obviously the energy change is much more significant. Both the yields of SF_6 and S_2F_{10} decrease, and since the SF_6 is much more sensitive to temperature, its rate of decline is much more rapid.

If the temperature is increased to 40°C, the yield of S_2F_{10} falls again. This might be predicted since at 15 cc./min. at 0°C nearly enough energy is already available for complete fluorination and the decrease in the number of S_2's will be much more significant. The SF_6 will increase because

of the large amount of thermal energy present. The changes in SF_6 and S_2F_{10} are, of course, accompanied by a decrease in the lower fluorides.

Since the more rapid reaction rate at 30 cc./min. of fluorine will provide a larger source of energy from the start, variations in the temperature of the reaction vessel will result in less significant changes in the yields of the products. Trends in the yields of SF_6 and lower fluorides which are similar to those at 15 cc./min. are observed as the temperature is lowered from 0°C to -40°C. However, as shown in the figure, the gradients of each curve are much more moderate due to the large amount of energy derived from the reaction itself.

Since the number of S_2's at 30 cc./min. of fluorine is not yet approaching its limiting value, a decrease in temperature will result in a more rapid increase of these fragments than would be expected at 15 cc./min. This will partially compensate the decreased energy available for activation and will result in a much slower decrease in S_2F_{10} yield than at 15 cc./min. Although no runs were done at -40°C at 60 and 90 cc./min. of fluorine, it can be predicted from the curves that the changes in these curves would be even less, and the 90 cc./min. series would probably produce a higher yield at this temperature.

These same considerations apply to the increase in temperature above 0°C. At the higher fluorine flow rates, the temperature of the reaction vessel will be much less

effective in determining the various yields. Thus, the yields of S_2F_{10} show very little change from 0 to 90°C in all the curves, and the gradients in SF_6 become much less rapid as the fluorine is raised from 30 to 90 cc./min. of fluorine.

It is interesting to note the very small changes in lower fluoride yields from 45 to 90°C irrespective of the fluorine rate. This indicates that enough heat is provided at 45°C to ensure fluorination of both S_1 and S_2 fragments. Further trends in the S_2F_{10} curves at these temperatures will be due to a change in the S_2/S_1 ratio. It can be seen that the yields of lower fluorides tend to become asymptotic at the same value and do not decrease to zero. Apparently a small percentage of the lower fluorides (which could include compounds such as SOF_2) is not capable of further fluorination to SF_6 or S_2F_{10}.

If the yields at 45 and 90°C are examined in the light of a fluorine variation, it will be seen that decreased rates of fluorine flow result in the same trends shown at 0°C. However, from the above considerations, it is evident that the yields of S_2F_{10} will generally be less at the higher temperatures and the maximum possible yield will decrease as the temperature is raised.

Since enough activation energy is present at 45°C for fluorination of the fragments, these curves show very little change in lower fluorides with variation in fluorine flow.

If the mechanism described above is to be complete,

it must account for the manner in which the formation of S_2F_{10} and SF_6 is inhibited by the action of oxygen. In Section III it was shown that a correlation existed between these yields and the production of oxyfluorides such as SO_2F_2 and SOF_2. Decreased amounts of S_2F_{10} were invariably accompanied by high yields of SO_2F_2 and the production of SF_6 was similarly affected by the formation of a lower fluoride which was tentatively assumed to be SOF_2. This was substantiated by the high yields of S_2F_{10} and SF_6 obtained in the leak-proof, comparatively oxygen-free system used in Section IV.

If the assumption is made, as before, that the formation of S_2F_{10} and SF_6 is contingent on the initial production of S_2 and S_1 fragments, then the oxygen must act to prevent the complete fluorination of these groups. Trautz and Ehrmann have reported that S_2F_2, in the presence of a spark and oxygen, decomposes to SOF_2 and SO_2 (15). Moissan and Lebeau (26) have also shown that SO_2 will react with fluorine to give SO_2F_2 and a little SOF_2. Since S_2F_2 is a very likely S_2 fragment, this decomposition in the presence of oxygen will result in a decreased rate of formation of S_2F_{10} and will represent a potential source of SOF_2 in the lower fluorides and SO_2F_2 in the remaining products, at the expense of the S_2F_{10}. If it is further assumed that progressive fluorination to SF_6 is also inhibited by the reaction of S_1 fragments with oxygen to form SOF_2, the experimental results can now be completely explained.

Examination of Table X and Figure 12 shows that the

addition of O_2 results in a decreased yield of S_2F_{10} which is accompanied by increased amounts of SO_2F_2. Since the yields of the oxyfluoride reach a limiting value at the same point as that at which the S_2F_{10} yield shows no further decrease, it seems possible that the SO_2F_2 is formed by the mechanism suggested above and that its yield is related to the number of S_2 groups available. Simultaneously the production of SF_6 will be inhibited since S_1 groups which would normally have been completely fluorinated will react to form SOF_2. This will result in the sharp increase in lower fluorides shown in the figure.

Since large volumes of SO_2F_2 correspond to only a small volume of oxygen, it is not surprising that the action of oxygen on the yield of S_2F_{10} is most effective at added amounts of less than 10 cc./min.

Fluctuations in the yields of the various products, similar to the effect shown with oxygen, are found when moisture is present in the system. This was first suspected by Lossing and Mungen (12) and was confirmed following investigation of the unpredictable behaviour in the large reaction tube under different conditions.

The moisture effect was not studied in detail, but the following suggestions are made to indicate a possible mechanism for the reaction.

Trautz and Ehrmann (15) have reported that S_2F_2 reacts with moisture in the following manner

$$2S_2F_2 + 2H_2O \longrightarrow 2H_2F_2 + SO_2 + 3S$$

As suggested in discussing the oxygen effect, the SO_2 can react to form SO_2F_2 and the formation of S_2F_{10} will be inhibited by this side reaction. The results in the large reaction tube indicate that the production of SF_6 is also critically affected by moisture with a resultant increase in lower fluorides. It must be emphasized that very little is known of this mechanism and these suggestions are only offered as a tentative hypothesis.

The mechanism outlined above has assumed throughout that the formation of S_2F_{10} is contingent on the presence of an S_2 linkage. However, suggestions have been made by other workers that an S_1 fragment could be progressively fluorinated to "radicals" such as SF_5 which could combine to form S_2F_{10}. The various possibilities and probabilities of this type of mechanism will now be discussed in detail.

Assuming, for the moment, that only S_1 fragments are present, the synthesis of S_2F_{10} can proceed through several paths. Since SF_6 and SF_4 are both known to exist, it might appear that combination of these compounds would be the most obvious method of preparation from S_1. A reaction of this type has been attempted in this laboratory. Since the lower fluorides are believed to contain some SF_4, they were added to pure SF_6 and the gases were subjected to high pressures. No S_2F_{10} was produced. This is not surprising since SF_6 is very stable and would require a very large amount of energy for reaction so that even if S_2F_{10} were formed,

decomposition would probably occur.

Another possible path would be the reaction of two SF_4's with F_2 to form S_2F_{10}. Since this involves a termolecular collision which is extremely unlikely, this mechanism is not considered feasible. However the combination of two SF_4's with subsequent attack by fluorine is more plausible and involves the fluorination of an S_2 linkage. This will be discussed in more detail later.

All other mechanisms in which S_2F_{10} is formed by S_1 fragments will ultimately require the combination of two SF_5 groups. Laidler has said that this is very unlikely (34). Furthermore, since collisions between sulphur and fluorine atoms or fluorine and fluorine atoms will be ineffective, the probability of formation of S_2F_{10} will be very small.

Another factor affecting the formation of S_2F_{10} from two SF_5 radicals will be the further possibility of an SF_5 being fluorinated to SF_6. It is evident that, disregarding energy considerations, a successfully orientated collision will be much more probable with SF_5 and fluorine than with two SF_5's because of steric factors.

The observed effect of an inert gaseous diluent gives further evidence of the improbability of this mechanism. The addition of nitrogen would decrease the concentrations of the fluorine and the various fragments in the vapor phase. Although, as mentioned before, Mass Law considerations are not strictly applicable, the rate of formation of S_2F_{10} should decrease by

a factor related to the square of the concentration of the SF_5 fragments. However, the experimental evidence shows an initial increase in the yield of S_2F_{10} with increased nitrogen dilution. It would be improbable that the mechanism involving combination of SF_5 radicals could account for this increase.

In discussing the fluorination and combination of single sulphur fragments, it is very significant that despite numerous attempts in the laboratory, no one has yet succeeded in producing even a trace of S_2F_{10} from the fluorination of compounds containing a single sulphur.

From both theoretical and experimental considerations, therefore, it seems that S_2F_{10} formation involves an S_2 linkage.

It has also been suggested that the reaction proceeds in the following manner. The reaction of fluorine with an S - S group will release sufficient energy to break that bond, but recombination can occur and fluorination can proceed progressively. Thus, for example, S_2F_2 could be fluorinated to S_2F_4 which would decompose into two SF_2 fragments. These fragments could then recombine and be fluorinated again to give S_2F_6 with similar decomposition. In any case, the ultimate product will be S_2F_{10}. If these fragments do not combine symmetrically or if they are fluorinated before collision with a similar fragment, the final product could be SF_6 or lower fluorides.

However, the number of collisions involved in this hypothesis would indicate that this mechanism is improbable.

Combination of the fragments will only occur if the two sulphurs are involved and will be ineffective if the fluorine atoms collide. The chance of two SF_2 fragments being orientated so that their collision will result in recombination to form S_2F_4 is therefore only one in nine. This chance becomes progressively smaller as the fragments become more completely fluorinated. In addition, numerous side reactions are possible which would tend to reduce further the probability of a successful collision.

The most probable path for the formation of S_2F_{10}, then, involves a mechanism essentially similar to the one developed in this thesis. With this in mind, the following calculation is of interest.

Assuming that S_2F_{10} can only be formed by fluorination of an S_2 linkage, a calculation has been made of the maximum possible yield under present reaction conditions. The method used is analogous to that reviewed by Mark in discussing the mechanism of the breakdown of long polymer chains (42).

It is assumed that there are n identical linkages in the original sulphur molecule. If a of these links are ruptured, the average degree of cleavage will be given by

$$\alpha = \frac{a}{n}$$

The probability of any of these bonds being ruptured will therefore be

$$\frac{a}{n} = \alpha$$

and the probability that it will remain intact will be $1 - \alpha$.

An i-membered group within the chain of sulphur atoms is now considered. In order that this group be split off intact, it is necessary that the bonds at the beginning and end of the group shall be ruptured, and that all bonds within the group (i - 1) remain unbroken. This probability will be

$$\alpha \cdot \alpha(1 - \alpha)^{i-1}$$

Since, in a two-membered group, i is equal to two, the probability of such a group being split off will be

$$\alpha^2(1 - \alpha)$$

For simplicity, an eight-membered molecule, such as exists in liquid sulphur, is chosen for a sample calculation of the maximum probability of formation of S_2 groups. This probability will depend on the average degree of rupture of the eight linkages. Thus, when one bond is broken $\alpha = \frac{1}{8}$, and hence the probability is

$$\frac{1}{8} \cdot \frac{1}{8} (1 - \frac{1}{8}) = 0.0137$$

When two bonds are broken, $\alpha = \frac{2}{8}$ and the probability is

$$\frac{2}{8} \cdot \frac{2}{8} (1 - \frac{1}{8}) = 0.0468$$

Similarly, probabilities can be calculated for further cleavage of the molecule. The maximum probability of formation of S_2 fragments is found to occur when five of the eight bonds are broken.

The relative probability of formation of an S_2 group in preference to S_1 or S_3 at this degree of cleavage can now be calculated. Since a negligible number of S_3, S_4---

groups is formed when five bonds are broken, the number of S_2 fragments formed by their decomposition is assumed to be negligible in relation to those obtained by direct cleavage of the eight-membered ring. The relative probability of S_2 formation on a weight basis leads to an optimum yield of 30.8 per cent S_2F_{10}.

Although fluorination of solid sulphur does not involve cleavage of a simple eight-membered ring, a similar calculation has shown that the optimum yield of S_2F_{10} does not vary significantly from 30 per cent, regardless of the number of sulphur atoms in the molecule.

It should be noted that the calculation assumes that the formation of an S_2 fragment involves cleavage of only two bonds, viz., those at the ends of the fragment.

Since no yield of S_2F_{10} greater than 30.7 per cent has ever been obtained from fluorination of sulphur, this calculation seems to give further support to the assumption that the production of S_2F_{10} is contingent on the presence of an S_2 fragment.

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CLAIMS TO ORIGINAL RESEARCH

Claims to original work

A method of production of disulphur decafluoride by the fluorination of sulphur using solid and gaseous diluents was developed.

An apparatus was constructed for the production and fluorination of a sulphur smoke of known concentration, and the effect of temperature and rate of fluorine flow was studied in this system.

The effects of variation in solid and gaseous diluents, rate of fluorine flow, and temperature were investigated with the solid sulphur system.

The critical effects of oxygen and moisture on the yields of disulphur decafluoride and sulphur hexafluoride were examined, and suitable modifications were introduced to reduce these factors.

An accurate method of analysing the gaseous products for SF_6, S_2F_{10} and SO_2F_2 has been devised, and procedures have been introduced for the determination of fluoride and sulphate ions in the caustic bubblers.

A mechanism of the reaction has been proposed which explains and correlates the results obtained.

Contributions to knowledge

Yields of S_2F_{10} as high as 30.7 per cent based on sulphur reacted can be obtained by the fluorination of sulphur using both solid and gaseous diluents.

The fluorination of a sulphur smoke dispersed in nitrogen gives yields of S_2F_{10} of 5 to 10 per cent on sulphur.

The yields of S_2F_{10} and lower fluorides are increased by decreased rates of fluorine flow, by dilution of the sulphur with sodium fluoride or copper powder, and by dilution of the fluorine stream with nitrogen. At very high nitrogen dilutions the yield of S_2F_{10} passes through a maximum and then decreases. Concomitant with these changes, the yields of SF_6 are decreased.

At low fluorine rates, the yield of S_2F_{10} passes through a maximum with change in temperature. The effect of temperature becomes less significant at low fluorine rates.

The production of SF_6 and S_2F_{10} is inhibited by small amounts of oxygen and moisture.

It is assumed that the formation of S_2F_{10} is contingent upon the presence of a fragment containing an S - S linkage, whereas SF_6 is formed by the fluorination of a single sulphur fragment. The relative proportions of these two types of fragments are assumed to be dependent on the temperature at the point of reaction.

More energy in the gas phase is required for the production of SF_6 than S_2F_{10}, and, in either case, if this energy is not available, lower fluorides will be formed.