THE STRUCTURES OF $SF_4.BF_3$ AND SOME RELATED COMPOUNDS

AN INVESTIGATION OF THE STRUCTURES OF $SF_4.BF_3$ AND SOME RELATED COMPOUNDS BY MEANS OF F^{18} TRACER STUDIES AND INFRA-RED AND F^{19} N. M. R. SPECTROSCOPY

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SCOPE AND CONTENTS:

The objective of this work was to investigate the structures of $SF_4.BF_3$ and some related complexes and to investigate the general usefulness of F^{18} tracer studies as an experimental tool in fluorine chemistry.

Methods have been developed for preparing BF_3^{18}, PF_5^{18}, AsF_5^{18}, SiF_4^{18} and SF_4^{18}. The structure of $SF_4.BF_3$ has been studied employing F^{18} tracer, infra-red and F^{19} N.M.R. techniques. The evidence obtained from the first two methods shows that $SF_4.BF_3$ has a fluorine bridged structure. The F^{19} N.M.R. investigation of the HF solutions of $SF_4.BF_3$ and SF_4AsF_5 indicates that these complexes ionize into SF_3^+ and the corresponding anion. The F^{18} exchange reactions of $SF_4.PF_5$, $SF_4.AsF_5$, $SeF_4.BF_3$ and $POF_3.BF_3$ have been studied. The evidence shows that these complexes are either ionic or fluorine bridged.

Evidence has been obtained from F^{18} tracer, infra-red and N.M.R. techniques that SF_4 and SiF_4 interact at low temperatures to form the adducts $SiF_4.SF_4$ and $SiF_4.(SF_4)_2$.

The formation of POF_4^-, SOF_3^- and 1:1 adduct of SF_4 and tetrahydrofuran has been demonstrated.

An analytical procedure has been developed for the determination of SO_4^{2-} in the presence of soluble silicates.

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CHAPTER 1

INTRODUCTION

The main purpose of this work was to investigate the structures of SF_4BF_3 and some related complexes. A number of available techniques were employed in this work of which the principal one was the use of F^{18} as a tracer. It was also an objective of the work to investigate the general usefulness of F^{18} tracer studies as an experimental tool in fluorine chemistry. Some of the relevant chemistry of the fluorides studied in this work are given in this chapter. The preparation, counting technique, and previous applications of F^{18} are described in Chapter 2.

Sulphur Tetrafluoride

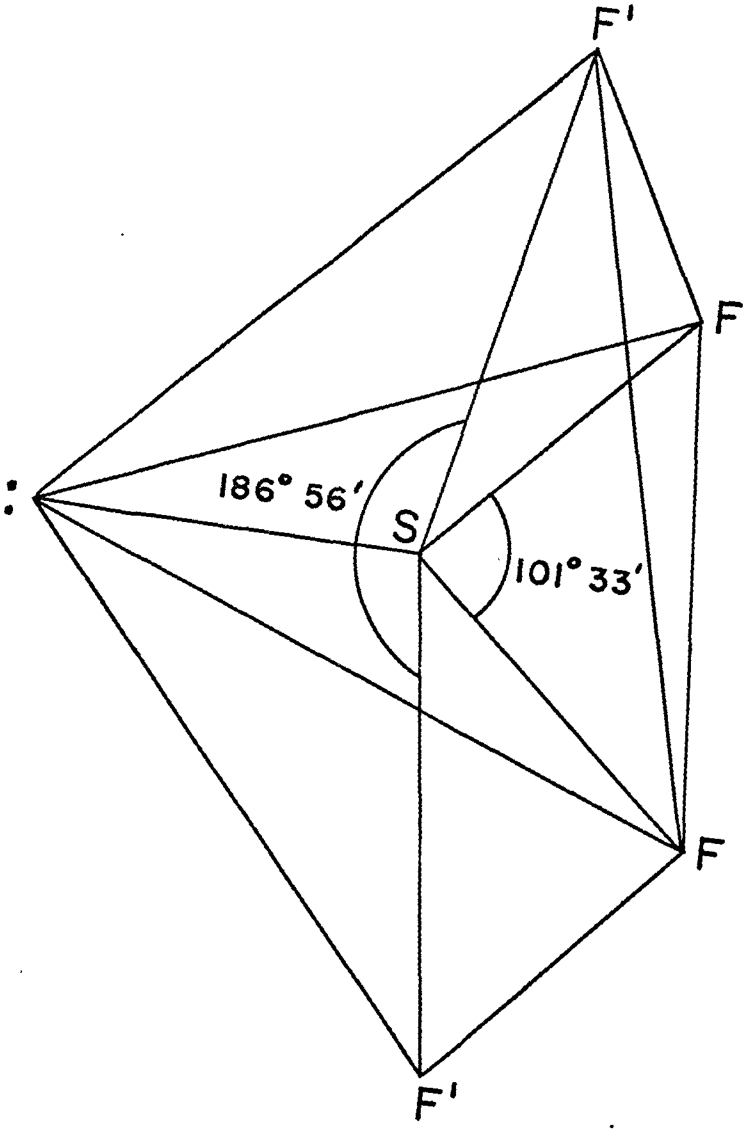
Sulphur tetrafluoride, described by Sidgwick1) as "almost certainly wrong", was isolated and characterized by Brown and Robinson2). It is conveniently made by refluxing $SC\ell_2$ with sodium fluoride in acetonitrile3). It is a colourless gas which condenses to a colourless liquid. A Trouton constant of 27.1 indicates that it is associated. The physical constants of SF_4 are given in Table 1.

The first information on the structure of SF_4 was obtained from its infra-red and Raman spectra4), which indicate C_{2v} symmetry. Subsequently these observations were confirmed by F^{19} nuclear magnetic resonance studies5,6) which showed that SF_4 molecule has two non-equivalent sets of fluorine atoms. The structure shown in Fig.1 was

TABLE 1

Melting and Boiling Points of Co-valent Fluorides

Compound	Melting Point	Boiling Point	Ref.
BF_3	-127.1°	101.0°	8,9)
SiF_4	-90°	-95.1° (sublimes)	9,10)
POF_3	-39.8°	-39.4°	9,11)
PF_5	-93.8°	-84.6°	9,11)
AsF_5	-79.8°	-53.2°	9,11)
SOF_2	-129.5°	-43.8°	9,12)
SF_4	-121.0 ± 0.5°	-40.4°	2,9,13)
SeF_4	-9.5°	106°	13,14)



$S-F = 1.545\ \text{A}^\circ$

$S-F' = 1.646\ \text{A}^\circ$

$F\hat{S}F = 101^\circ\ 33' \pm 30'$

$F'\hat{S}F' = 186^\circ\ 56' \pm 30'$

FIG: 1

subsequently obtained from microwave studies7). It has been suggested that the bonding in the molecule can be described in terms of a trigonal bipyramidal set of $sp^3d_{z^2}$ hybrid orbitals7) on the sulphur atom one of which is occupied by a non-bonding or lone pair of electrons. The difference in the lengths of the equatorial and axial bonds has been supposed to be consistent with the idea that the equatorial bonds are formed by sp^2 hybrid orbitals while the axial bonds are formed by pd_{z^2} hybrid orbitals. An alternative explanation of the shape of SF_4 molecule is that it is determined by the interaction of the five electron pairs of the valency shell of the S atom, which give a trigonal bipyramidal arrangement with the lone pair in an equitorial position5,15).

Sulphur tetrafluoride is readily hydrolysed to SO_2 and HF via SOF_2 by aqueous media. Although sulphur tetrafluoride is hydrolysed very rapidly it can be handled and manipulated in glass equipment, provided that the glass has been thoroughly dried under vacuum.

Compounds containing hydroxyl groups react readily with SF_4. Carboxylic acids and sulphonic acids are converted to acid fluorides while alcohols give the corresponding fluorocarbons16).

Sulphur tetrafluoride also reacts with compounds containing a carbonyl group16) such as aldehydes, ketones, carboxylic acids, and their derivatives, the oxygen atom being replaced by two fluorine atoms. The fluorinations of the carboxyl group is very specific; for example unsaturated carboxylic acids may be fluorinated without affecting the the unsaturated bond

$$CH \equiv C\,COOH \xrightarrow{SF_4} CH \equiv CC\,OF \xrightarrow{SF_4} CH \equiv CCF_3$$

Other functional groups including fluoro, chloro, bromo and nitro are usually unaffected by SF_4 at temperatures up to 160°[16]. Carboxylic esters react with SF_4 under forcing conditions. Thus methyl benzoate did not react at 250°, but at 300° yielded benzotrifluoride and methyl fluoride[16].

$$C_6H_5COOCH_3 + 2SF_4 \longrightarrow C_6H_5CF_3 + CH_3F + 2SOF_2$$

Perfluoroalkylethers[16] have been obtained by reacting corresponding fluoroesters with SF_4.

Sulphur tetrafluoride is a useful reagent for the preparation of other inorganic fluorides from the oxides and sulphides. This general reaction is characterized by replacement of oxygen or sulphur to give the corresponding fluorides or oxyfluorides[1,17]. It has been successfully employed for the preparation of UF_6, UF_4, PuF_6 and PuF_4.

At temperatures up to 300°, SF_4 does not react with chlorine[18], however, sulphur chloropentafluoride[19] is produced when SF_4 is heated to 100 - 350° with $C\ell F$ or $C\ell F_3$.

Sulphur tetrafluoride reacts with $BC\ell_3$ at -73°, at this temperature no evidence of complex formation has been obtained. Instead SF_4 functions as a fluorinating agent[18]. If SF_4 is in excess the principal reaction is the following:-

$$7SF_4 + 4BC\ell_3 \longrightarrow 4SF_4{\cdot}BF_3 + 3SC\ell_2 + 3C\ell_2$$

but mixed halides of boron result if $BC\ell_3$ is in excess.

$$3SF_4 + 8BC\ell_3 \longrightarrow 3SC\ell_2 + 3C\ell_2 + 4BF_2C\ell + 4BFC\ell_2$$

Sulphur tetrafluoride is oxidised to SF_6 by fluorine. It does not react with oxygen alone, but in the presence of NO_2 it is oxidised to SOF_4 20). Strong oxidizing agent such as CrO_3, Na_2CrO_4, K_2CrO_4, MnO_2, $C\ell O_2$, PbO_2, $NaNO_2$ and $NaNO_3$ also oxidise SF_4 to SOF_4 20).

The interaction of SF_4 with tertiary amines 21) and $(CH_3)_4NF$ 22) to form stable addition complexes $(CH_3)_3NSF_4$ and $(CH_3)_4$-NSF_5 shows that it is a Lewis acid.

Bartlett and Robinson 23-25) have reported that SF_4 forms a series of solid complexes with certain inorganic fluorides that are fluoride ion acceptors. These complexes, viz: $SF_4 \cdot BF_3$, $SF_4 \cdot AsF_5$ and $SF_4 \cdot SbF_5$, written in the ascending order of their stability, were prepared by condensing together the two constituents in stoichiometric amounts and then warming to ordinary temperature. Later a number of similar complexes $SF_4 \cdot PF_5$, $SF_4 \cdot AsF_3$ and $(SF_4)_2 \cdot GeF_4$ were reported by Muetterties, et al. 17,26).

The structures of these complexes are not known with certainty. Bartlett and Robinson 23,24) postulated that they were simple Lewis acid-Lewis base adducts. Later workers 1,18) argued that this formulation is not correct and suggested that they were ionic complexes of the type $SF_3^+ \ BF_4^-$. However, the experimental evidence in favour of the ionic formulation was not conclusive.

$SF_4.BF_3$

Of all these molecular adducts only $SF_4 \cdot BF_3$ has been investigated extensively. The molecular complex $SF_4 \cdot BF_3$ is a white solid which sublimes at 80° under atmospheric pressure and is decomposed by dry ethers23-25), viz: methyl ether, ethyl ether, aninsole and tetrahydrofuran (THF)

$$SF_4 \cdot BF_3 + \begin{matrix} R \\ R \end{matrix} \rangle O = \begin{matrix} R \\ R \end{matrix} \rangle O \rightarrow BF_3 + SF_4$$

When vapours of $SF_4 \cdot BF_3$ are passed over heated sodium fluoride SF_4 is set free and BF_3 is retained by NaF as $NaBF_4$23-25).

Examination of the infra-red spectrum of the gaseous compound indicates that it is at least 95% dissociated into BF_3 and SF_4 at room temperature18). This was confirmed by measurement of vapour density at room temperature from which an apparent molecular weight of 85 ± 5 was calculated. The average of the molecular weights of SF_4 and BF_3 is 88.

The vapour pressure of $SF_4 \cdot BF_3$, given in Table 2, was determined by Seel and Detmer27). By extrapolating the $\log p$ vs $\frac{1}{T}$ curve of $SF_4 \cdot BF_3$ it was found that at about -50° the vapour pressure of $SF_4 \cdot BF_3$ becomes negligible (Fig.2).

Boron Trifluoride

Boron trifluoride is a colourless gas which condenses to a colourless mobile liquid. The boron trifluoride molecule has a planar trigonal structure with the fluorine atoms at the corners and the boron atom at the centre 8,9,28-34).

Table 2

Vapour Pressure of $SF_4 \cdot BF_3$[27)]

Temperature °K	$\frac{1}{T}$	Pressure in mm of Mercury
274	0.003649	16
284.5	0.003521	36
292	0.003425	64
301	0.003322	124
306	0.003268	177
310.7	0.003218	237
314.6	0.003179	311
317.8	0.003146	377
323	0.003096	522
325.1	0.003076	610
328.9	0.003040	751

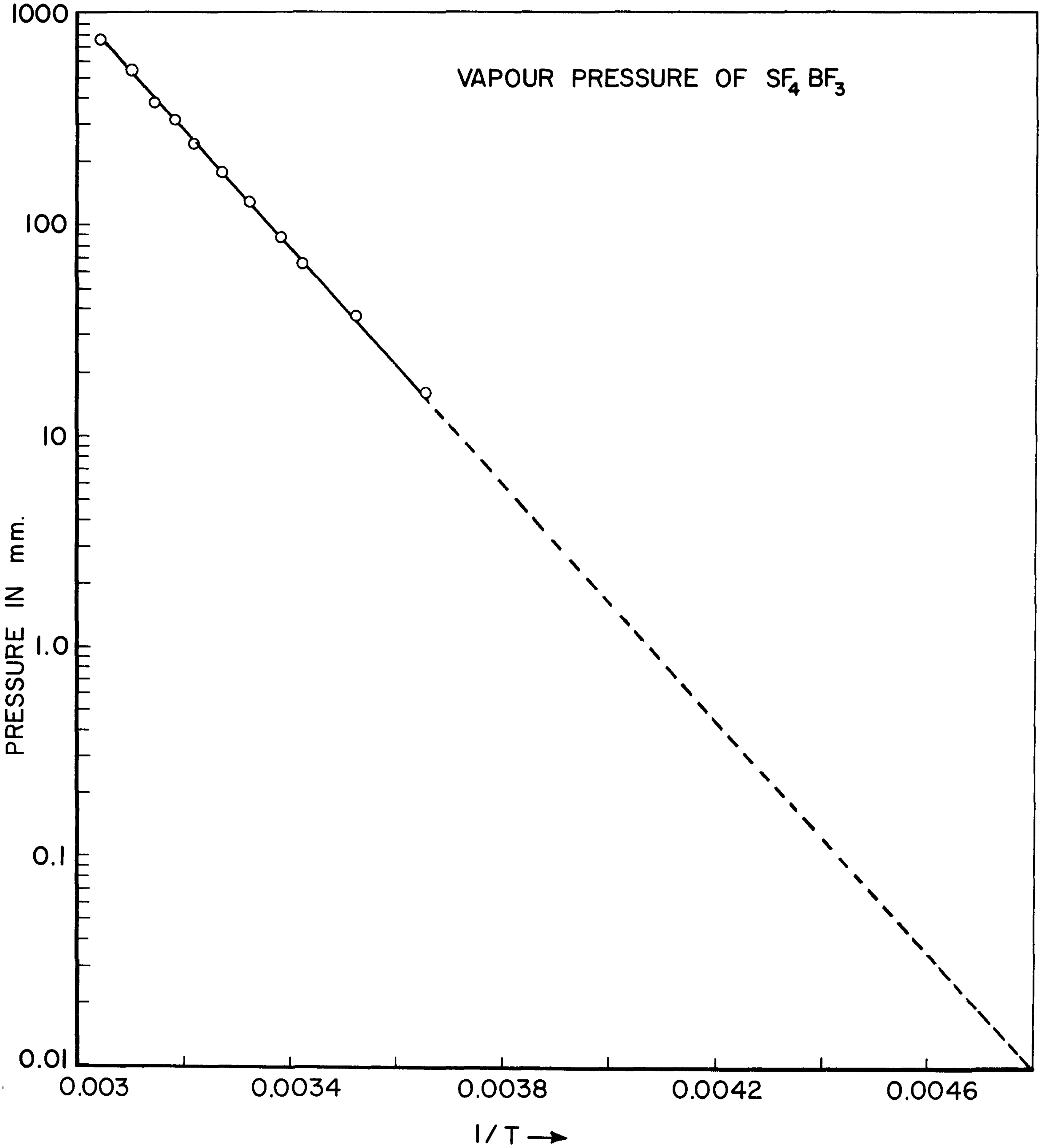

VAPOUR PRESSURE OF $SF_4 BF_3$
PRESSURE IN mm.
1000
100
10
1.0
0.1
0.01
0.003
0.0034
0.0038
0.0042
0.0046
1/T →

FIG: 2

Boron trifluoride is one of the most powerful acceptor molecules known, and it forms a very large number of co-ordination compounds. It is capable of combining with both inorganic and organic molecules containing donor atoms, e.g. O, N and S. The structures of many of these co-ordination compounds are not known. The inorganic complexes of boron trifluoride can be classified as follows:-

(1) Ionic complexes containing BF_4^- ion such as $LiBF_4$ $NaBF_4$, $NOBF_4$, $Zn(BF_4)_2.6H_2O$, $Co(NH_3)_6\ (BF_4)_2$ and $Mn(BF_4)_2.6H_2O$ etc. The alkali metal fluoroborates split off BF_3 at temperatures above 200°, but the others decompose more easily, often at temperatures below 100°[34,35].

(2) Co-ordination compounds of boron trifluoride with sulphates and phosphates etc., e.g. $Na_2\ SO_4.BF_3$, $CoSO_4.2BF_3$, $FeSO_4.BF_3$, $Na_3\ PO_4.3BF_3$ and $K_2P_2O_7.4BF_3$. All the co-ordination compounds of this series are stable and decompose only at temperatures above 300°. Structures have been suggested for these compounds, but they have not been established experimentally[34].

(3) Boron trifluoride also forms thermally unstable addition products with H_2S, SO_2, SO_3, POF_3, PH_3, SF_4, SeF_4 and TeF_4[23-25,34,36]. The compounds are generally stable at low temperatures and their structures have not been investigated.

Selenium Tetrafluoride

Selenium tetrafluoride was prepared by Aynsley, Peacock and Robinson[14] by the reaction of fluorine, diluted with nitrogen, on a thin layer of selenium at 0°. It is a colourless liquid at ambient temperature. Its melting and boiling points are given in Table 1.

The SeF_4 molecule has been assigned a distorted tetrahedral structure as a result of an electron diffraction study[28,37)] with Se - F 1.756A°, two (opposite) bond angles of 120(10°), and the remainder 104°. On the other hand, the Raman spectrum of the vapour[28,38)] has been interpreted as indicating a configuration derived from a trigonal bipyramid like that of SF_4. By analogy with SF_4 and on general theoretical grounds this seems to be the most probable structure.

Selenium tetrafluoride reacts rapidly with traces of moisture forming $SeOF_2$ and HF. It is miscible with H_2SO_4, ether and IF_5 and dissolves appreciable quantities of $CC\ell_4$, $CHC\ell_3$ bromine, iodine, sulphur and selenium[14)]. It has been reported that SeF_4 dissolves fluorides of $T\ell^+$ and alkali metals except lithium to form complexes of the type $MSeF_5$[14)]. Robinson, et al.[39)] have also reported the formation of nitronium-penta-fluoro-selenium NO_2SeF_5. Peacock[40)] has reported that SeF_4 slowly attack glass and reacts with metallic mercury to form $HgSeF_4$. It reacts vigorously with $KMnO_4$[40)] and $BC\ell_3$[25)], the reaction products are $KMnF_5$, $SeOF_2$ and oxygen in the former case and BF_3 and $SeC\ell_4$ in the latter. Selenium tetrafluoride reacts with fluorine and SeO_2 to form SeF_6 and $SeOF_2$ respectively.

An ether complex of pyridine-tetra-fluoroselenium (IV), $(C_5H_5N)\cdot SeF_4$, $(C_2H_5)_2O$ has been reported by Anysley and Hetherington[41)].

Selenium tetrafluoride reacts with VOF_3 and SO_3 to form $VOF_3 \cdot 2SeF_4$ and $SO_3.SeF_4$ respectively[40]. With the hexafluorides of osmium and iridium SeF_4 forms $OsSeF_9$ and $IrSeF_9$ respectively[13,42]. Robinson, et al.[23-25,43] and Seel et al.[27,44] have prepared the complexes $SeF_4 \cdot BF_3$, $SeF_4.AsF_5$, $SeF_4.SbF_5$, $(SeF_4)_2.GeF_4$, $(SeF_4)_2 \cdot PdF_4$, $(SeF_4)_2 \cdot PtF_4$, $SeF_4 \cdot AuF_3$ and $(SeF_4)_2 \cdot RhF_4$. All these complexes have a fair degree of thermal stability and they can be stored in sealed glass tubes at room temperature.

Selenium tetrafluorides replaces SF_4[25] from the complexes $SF_4 \cdot BF_3$, $SF_4 \cdot AsF_5$ and $SF_4 \cdot SbF_5$.

Phosphorus Pentafluoride and Arsenic Pentrafluoride

The pentafluorides of phosphorus and arsenic have very strong affinity for oxygen and nitrogen compounds having even the slightest basic properties. They also form complexes by accepting fluoride ion. These pentafluorides have trigonal bipyramid[9,28] structures and their complexes, formed either with a donor molecule or a fluoride ion, are octahedral.

A large number of molecular complexes of PF_5 and AsF_5 with organic bases such as ethers, tertiary amines, sulphoxides, nitriles, amides, and aromatic hydrocarbonds, have been reported[45-51].

The compounds of inorganic fluorides with PF_5 and AsF_5 are relatively few. It is known that these pentafluorides react with NOF, NO_2F, alkali metal fluorides, $C\ell F_3$, $C\ell O_2$, $C\ell O_2F$, $1F_7$, SF_4 and SeF_4[13,23-26,52-56].

The complex $SF_4 \cdot AsF_5$ [25)] has very little vapour pressure at room temperature and sublimes when warmed in vacuum; at 180° the vapour pressure of the complex is about one atmosphere. Freshly prepared $SF_4 \cdot AsF_5$ is white, but rapidly becomes pale blue. The adduct $SF_4 \cdot PF_5$ is also white and does not change colour, its vapour pressure at room temperature was found to be between that of $SF_4 \cdot BF_3$ and that of $SF_4 \cdot AsF_5$.

The melting and boiling points of the two compounds are given in Table 1.

Phosphorus Oxy Trifluoride

Phosphorus oxytrifluoride is a product of partial hydrolysis of PF_5. The melting and boiling points of the gas are given in Table 1. It does not attack dry glass upto 400^{o} [9)].

Electron diffraction studies have shown POF_3 to be tetrahedral, with a P-O distance close to 1.45A°, a P-F distance about 1.53A° and a XPX angle of 106^{o} [9,28,57)]. The tetrahedral structure is also evident from its Raman spectrum[9,58,59)].

In 1943 Booth and Walkup[8,36)] reported the results of the thermal analysis of $POF_3 - BF_3$ system. Due to experimental difficulties they could not investigate the mixture containing more than forty-three mole per cent of BF_3. From the decrease in the vapour pressures and the observed melting points of the mixtures of $POF_3 - BF_3$ they concluded that an addition compound $POF_3 \cdot BF_3$ was formed. By extrapolating the freezing-point curve they determined the melting point of the complex to be 20°. Topchieve et al.[34)] did not consider this evidence to be sufficient and have stated in their book "in no case could a definite compound be detected".

Larsen et al.[13,60)] showed that POF_3 forms addition compounds with the tetrachlorides of zirconium and hafnium. These compounds tend to decompose below or at the melting point. The compounds and the approximate melting points are $POF_3 \cdot ZrC\ell_4$, 85°, and $POF_3 \cdot HfC\ell_4$, 85°. The structures of these complexes have not been determined.

Thionyl Fluoride

Thionyl fluoride is prepared by the fluorination of $SOC\ell_2$ employing SbF_3 as the fluorinating agent[9,61)]. It is a colourless mildly fuming gas. It is thermally very stable and attacks glass at 400°[9)]. The melting and boiling points of thionyl fluoride are given in Table 1.

The SOF_2 molecule has a pyramidal structure, with S-F bond 1.585A°, S-O bond 1.412A°, FSF angle 92.8° and FSO angle 106.8°[28,62)].

Booth and Walkup reported a very unstable 1:1 addition compound, formed between SOF_2 and BF_3, melting at -140.8°[8,36)]

In a very recent publication Ruff and Lustig[63)] prepared SOF_4 by the fluorination of SOF_2. These workers have also postulated the formation of $CsSOF_3$.

Silicon Tetrafluoride

Pure silicon tetrafluoride is a colourless pungent gas which fumes in air. Its melting and sublimation points are given in Table 1. Its structure has been shown by electron diffraction[9,64)] to be tetrahedral. The Raman and infra-red spectra are in agreement with this structure[9,65]. The Si-F bond length has been found to be 1.56Å[28,66].

The reactions of SiF_4 with ammonia or primary and secondary amines are usually vigorous and are not well understood. Silicon tetrafluoride is capable of forming complexes with donor molecules or with fluoride ion. It forms many stable complexes with organic bases such as trimethyl amine, dimethyl formamide, dimethyl sulfoxide, pyridine[67] and ethylene diamine[68]. The structures of most of these complexes have been established, but in a few cases the nature of the bonding is not known, e.g. in $SiF_4 \cdot 2(CH_3)_2SO$ it is not known whether O or S is the donor. In 1936 it was briefly reported that SiF_4 reacts with alcohol in a 1:4 mole ratio yielding compounds stable at low temperatures[69]. Recently it has been confirmed that SiF_4 reacts with methanol in a 1:4 mole ratio forming the complex $SiF_4 \cdot 4CH_3OH$[70].

Silicon tetrafluoride reacts with alkali metal fluorides[71,72] barium fluoride and nitrosyl fluoride[52]. In all these complexes the SiF_6^{2-} ion has an octahedral configuration.

CHAPTER 2

Fluorine-18: Preparation and Applications

Introduction

Fluorine, as found in nature, has the distinction of being monoisotopic; its atomic weight is 19 and it is non radioactive. However, a number of its isotopes F^{16} 13,73-75) F^{17} 13,76-79) F^{18} 13,80-97) F^{20} 13,98-102) and F^{21} 13,103,104) have been synthesised by various nuclear reactions. These artificially produced isotopes are unstable, their half-lives and modes of decay are shown in Table 3.

The first three isotopes, which are neutron poor, decay by positron emission, whereas the last two, which are neutron rich, are β^- emitters105). All the radio-active isotopes of fluorine are short-lived, and this property probably accounts for their limited use in chemical investigations.

Only two isotopes of this element, viz: F^{18} and F^{20} have been used by chemists. The former has been successfully employed in a number of tracer studies and the latter has been used for determining micro amounts of fluorine by thermal neutron activation analysis.

Preparation of Fluorine-18

The production of fluorine-18 was first reported in 1937 by Snell80), who obtained it by bombarding neon gas with 5 Mev deutrons

TABLE 3

Fluorine Isotopes[13)]

Nuclide	Particles Emmitted	Product Nuclide	Half-life
F^{16}	β^+	O^{16}	10^{-19} sec.
F^{17}	β^+	O^{17}	60-72 sec.
F^{18}	β^+ (97%) E.C.(3%)	O^{18}	107-112 min.
F^{19}	stable	-	-
F^{20}	β^-	Ne^{20}	10-12 sec.
F^{21}	β^-	Ne^{21}	5 sec.

NOTE: E.C. = Electron Capture or K Capture and by Pool, Cork and Thornton81) as a product of the nuclear reaction, F^{19} (n,2n) F^{18}. Subsequently a large number of nuclear reactions were reported for the preparation of this isotope, but not all of them are of practical importance. A number of satisfactory methods are listed in Table 4.

Methods 3 and 7 appeared to be the most convenient since it was possible to use the McMaster nuclear reactor as a source of high neutron flux. Method 3 was in fact used because it gives a high yield of fluorine-18. In this method fluorine-18 is the product of a secondary reaction as shown by the following equations

$$Li^{6}_{3} + n^{1}_{o} \longrightarrow He^{4}_{2} + H^{3}_{1}$$

$$H^{3}_{1} + O^{16}_{8} \longrightarrow F^{18}_{9} + n^{1}_{o} .$$

Knight, et al.82) calculated that in this reaction the yield of F^{18} is approximately 2×10^{-5} F^{18} nuclei per triton produced. Thus, any impurity, even of small thermal neutron absorption cross-section would be capable of introducing very large spurious activities relative to the F^{18} produced by the triton reaction. Hence, radiochemical contamination constitutes a serious problem unless stringent precautions are taken regarding the purity of target material. To meet this requirement lithium carbonate was chosen for irradiation as this compound is available in a highly pure state. Moreover, it has high thermal and radiation stability. The fluorine-18 is obtained in the form of LiF^{18}. This labelled lithium fluoride was used for

TABLE 4

Useful Methods for Producing Fluorine-18[81)]

	Nuclear Reaction	Radiation Source	Target	Ref.
1.	$N^{14}(\alpha, \gamma) F^{18}$	1.2-2.2 Mev α^{++} from cyclotron or linear accelerator.	Tantalum nitride, magnesium nitride.	83)
2.	$O^{16} (d, \gamma) F^{18}$	1.1 Mev deutrons from cyclotron or linear accelerator.	Oxygen.	84)
3.	$O^{16} (t, n) F^{18}$	Nuclear reactor 2-6 Mev tritons from the reaction $Li^{6}(n, \alpha)t$.	Any combination of Li and O_2, e.g. Li_2CO_3, $LiNO_3$, Li_2O etc.	82,85)
4.	$O^{16} (He^{3}, p) F^{18}$	Cyclotron or linear accelerator 2 Mev $(He^{3})^{++}$	NiO.	86
5.	$O^{17} (p, \gamma) F^{18}$	Cyclotron or linear accelerator.	Oxide layer on various metals.	87

TABLE 4 (continued)

Useful Methods for Producing Fluorine-18[81)]

	Nuclear Reaction	Radiation Source	Target	Ref.
6.	O^{17} (d,n) F^{18}	Cyclotron or linear accelerator 1.7-3.7 Mev deutrons.	O_2, H_2O, WO_3, PbO, CO_2, NiO enriched to 0.89% O^{17}.	88)
7.	O^{18} (p,n) F^{18}	Cyclotron, linear accelerator or recoil protons produced during slowing down of fast neutrons in a nuclear reactor. 1.7 - 3.7 Mev protons.	Water with high concentration of O^{18}.	89, 90)
8.	F^{19} (n, 2n) F^{18}	Fast neutrons from cyclotron, or Li^6(d,n) Be^7 reaction.	LiF.	81)
9.	F^{19} (p,d) F^{18}	Cyclotron or linear accelerator 10 Mev protons.	Teflon, 11.9 mg/cm^2.	91)

TABLE 4 (continued)

Useful Methods for Producing Fluorine-18 81)

	Nuclear Reaction	Radiation Source	Target	Ref.
10.	F^{19} (d,t) F^{18}	Cyclotron or linear accelerator 9 Mev deutrons.	NaF, Teflon.	92
11.	F^{19} (γ,n) F^{18}	Betatron, 48-84 Mev photons.	KHF_2, LiF, CaF_2 etc.	93, 94)
12.	F^{19} (p,pn) F^{18}	Protons from cyclotron or linear accelerator.	AlF_3 or any compound of fluorine.	95)
13.	Ne^{20} (d,α) F^{18}	5 Mev deutrons from cyclotron or linear accelerator.	Neon	80)

labelling various gaseous fluorides by fluorine exchange and the spurious activities such as Na^{24} etc., present in the irradiated sample were not transferred to the labelled gas. Another added advantage of using lithium carbonate is that it can be used directly for the preparation of $LiBF_4^{18}$ 35,106), which is an intermediate in the preparation of boron trifluoride labelled with fluorine-18.

The approximate amount of fluorine-18 produced can be calculated from the following expressions. In these calculations it has been assumed that the tritons formed in the reaction, $Li^6(n, \alpha)t$, do not decay. Equation (1) gives the production rate of tritons. Equation (2) gives the amount of fluorine-18 at the end of the irradiation.

$$\frac{dN}{dt} = N_{Li} \quad \sigma_{Li} \quad \phi \tag{1}$$

where $\frac{dN}{dt}$ = rate of production of tritons

N_{Li} = number of Li^6 atoms in the target

σ_{Li} = absorption cross section of Li^6 for thermal neutrons in barns (10^{-24} cm^2)

ϕ = thermal neutron flux, neutrons/cm^2/sec.

$$A_F(t) = N_o \sigma T(1-e^{-\lambda t_1})\ e^{-\lambda t_2} \qquad (2)$$

where $A_F(t)$ = Number of disintegrations of F^{18} per second at the end of the irradiation period t.

N_o = Number of O^{16} atoms in the target.
T = Triton flux which is related to $\frac{dN}{dt}$ (Equation (1))*.
σ = Cross section for O^{16} (t,n) F^{18} reaction: approximately 112 mb.107).
λ = Decay constant of F^{18} = $\ln 2/T_{1/2}$ $T_{1/2}$ = half life of fluorine-18.

t_1 = Irradiation time in the same units as $T_{1/2}$.

t_2 = Time from end of irradiation to time of counting.

* Knight, et al.82) have suggested that

$$\sigma T = \frac{dN}{dt}\quad 2 \times 10^{-5}.$$

In the preparation of fluorine-18 several millicuries of tritium are also produced. It is present in molecular form adsorbed on the surface of Li_2CO_3. Since tritium73,108) decays by the emission of 0.0176 Mev β^- it does not constitute a potential health hazard as long as it is kept in a container. The β^- being very soft are completely absorbed by the walls of the vessel. During the preparation of BF_3^{18} or LiF^{18} it is set free and is allowed to escape into the laboratory exhaust system and subsequently into the atmosphere. The tritium is thus diluted to a concentration permissible by radiation Health Safety Regulations108).

Counting Equipment

A block diagram of the counting equipment is given in Fig.3.

- (a) Well Type Scintillation Detector - Baird Atomic - Model 810.
- (b) Linear Amplifier - Baird Atomic - Model 215.
- (c) Pulse Height Analyser - Single Channel-Atomic Instrument Company - Model 510.
- (d) Six Decades Scaler - Beckman/Berkeley - Model 2060.
- (e) Digital Recorder - Beckman/Berkeley - Model 1452.

When γ-rays are absorbed by the sodium iodide cyrstal of the detector, light is emitted whose intensity is proportional to the energy of the incident photon. Since sodium iodide is transparent to its own luminescence these light flashes can be detected and then amplified by a photomultiplier tube, preamplifier and linear amplifier. The resulting pulses are then fed into a pulse height analyser (selector) which selects the pulses corresponding to the photons of desired energy.

The equipment was standardised with the 0.662 Mev γ-ray from Cs^{137} source and the F^{18} counted using the 0.511 Mev γ-ray from the positron[96,97)] annihilation.

Production of Fluorine-18

A 100 mg sample of A.R. lithium carbonate dried at 120° was placed in a polystyrene vial. The vial was wrapped in a thin

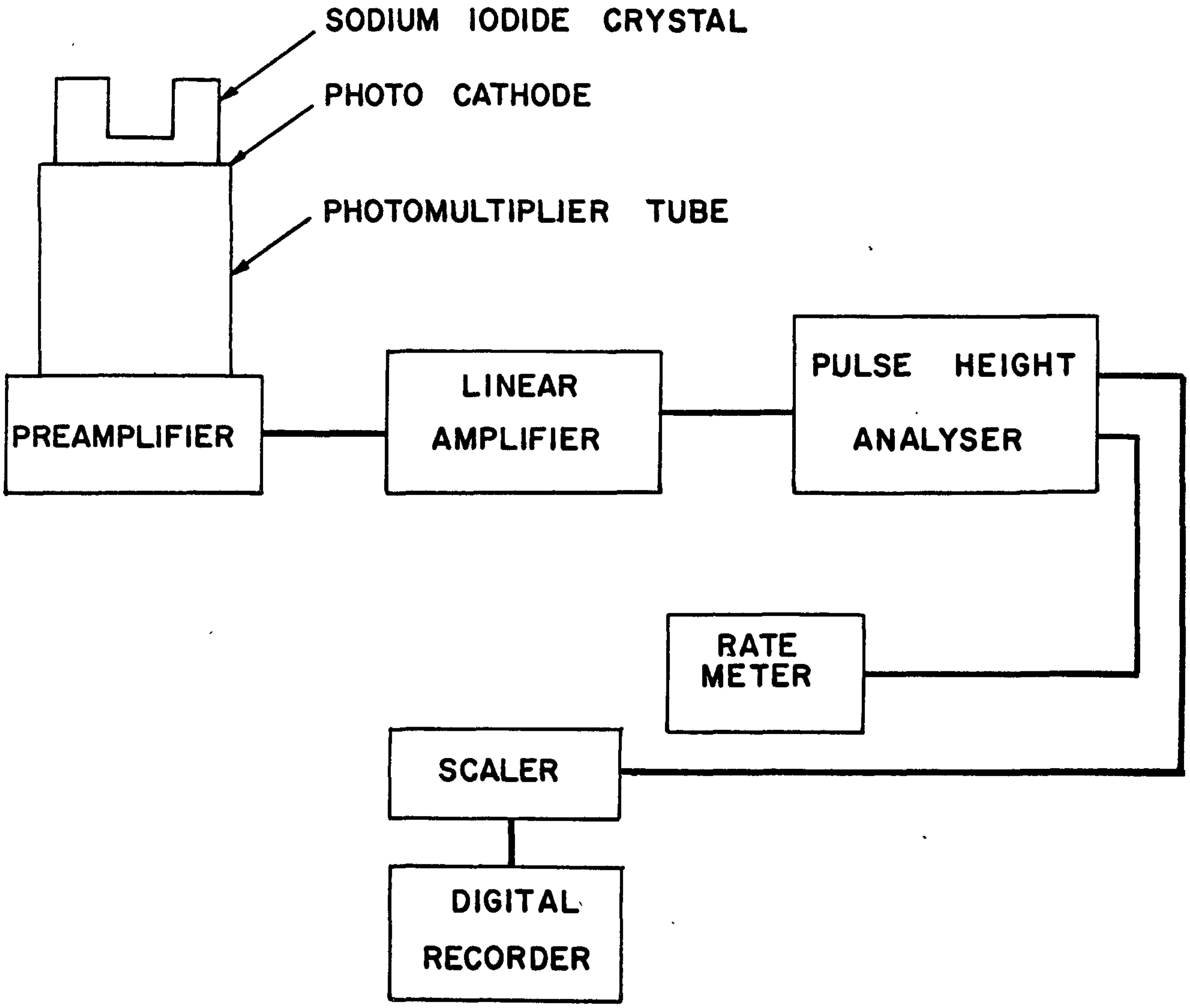

SODIUM IODIDE CRYSTAL
PHOTO CATHODE
PHOTOMULTIPLIER TUBE
PREAMPLIFIER
LINEAR AMPLIFIER
PULSE HEIGHT ANALYSER
RATE METER
SCALER
DIGITAL RECORDER

FIG: 3

aluminium foil and placed in a standard aluminium irradiation capsule. The capsule was irradiated with thermal neutron flux of the order of 10^{13} neutrons/cm^2/sec. After irradiation the sample was "cooled" for 30-60 minutes in order to allow the short lived activity of $A\ell^{28}$ to decay. The capsule was then opened in a glove box behind a lead shield and the sample was subjected to chemical treatment, as described in Chapter 3. The activity of F^{18} was between 0.05 - 0.1 mc.

The extraneous activities, mainly due to heavy metals and sodium-24, do not exchange with gaseous fluorides and hence these impurities did not constitute a radio active contamination problem. However, as a check the half-life of fluorine-18 was determined by the technique described below. It was found to be 109 ± 1 minutes in agreement with the literature. (Fig.4).

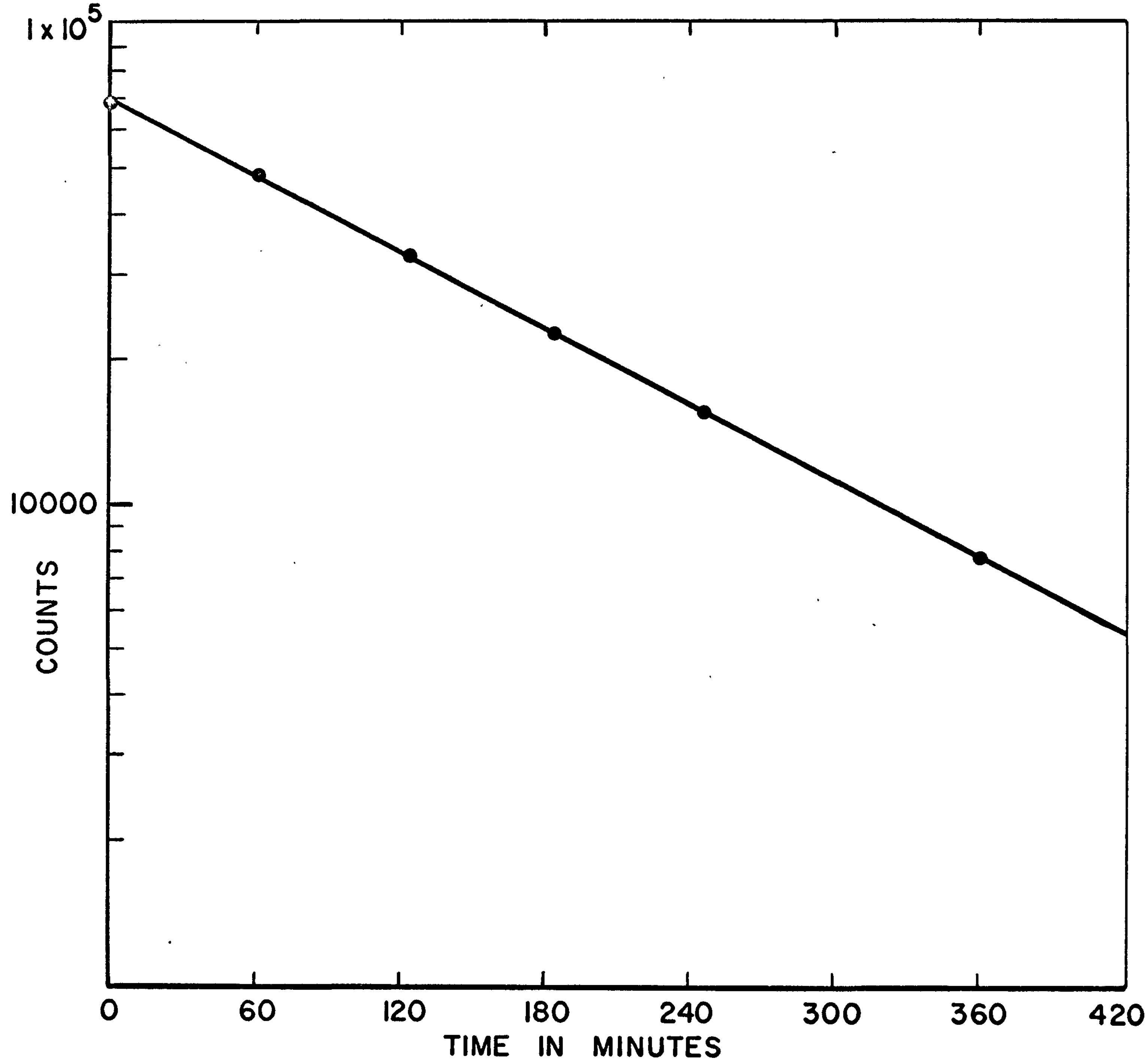
Counting of Fluorine-18

Fluorine-18 with half-life of 109.72 minutes109) decays to oxygen-18 by the emission of a 0.64 Mev positron. There are no unusual counting problems involved in the radio-chemical assay of F^{18} and any method normally used for detecting β^+ emmitters may be employed. This isotope can be detected and assayed by monitoring directly the β^+ or the 0.511 Mev annihilation γ-ray96,97). Both Geiger Muller (G.M.) tubes and scintillation detectors have been used for counting samples containing fluorine-18. It has been counted in the form of a solid, liquid or a gas. The solid samples can be prepared from any material which will form an insoluble fluoride precipitate. Knight, et al.[82,96] employed lead chlorofluoride precipitated from aqueous solution by the addition of hydrochloric acid and lead acetate. The sample was centrifuged washed and counted in the conventional manner.

Little attention has been given to the problem of precise assay of F^{18} in the liquid phase or in solution. Rogers and Katz[96,110] used an aluminium vessel to hold samples of liquid HF under its own vapour pressure at room temperature. A thin walled mica end-window type G.M. counter was placed adjacent to the bottom of the chamber. It was not possible to fill the holder reproducibly which resulted in poor precision.

Most of the precise counting of F^{18} has been done in the gas phase. Dodgen and Libby[111] used a counter with 0.01 inch aluminium wall contained in a brass jacket and sealed with a teflon gasket. Labelled hydrofluoric acid or fluorine was admitted to this chamber. For samples filled at 0.5 atm counting rates of the order of 1,000 to 5,000 cpm were normally obtained. All the activities were corrected for decay and extrapolated back to a convenient initial time using a half life of 110 minutes[96,111]. Individual specific activities were quoted with an uncertainty of about ±2 per cent.

Rogers and Katz[110] also assayed F^{18} in the form of gaseous HF, $C\ell F_3$ and BrF_5. The gases were contained in a copper vessel, about 6000 $m\ell$ capacity, in which a Victoreen 1B85 aluminium Thyrode detector was situated. Weighed samples of HF^{18}, $BrF_3{}^{18}$ $BrF_5{}^{18}$



HALF LIFE OF FLUORINE - 18

FIG : 4

were introduced into the chamber for the determination of specific activity. For a gas sample filled at pressures in the region of one atmosphere count rates of the order of 5,000 to 10,000 cpm were obtained. One of the important sources of error in the assay of F^{18} was the rather high background in the counter due to exchange of F^{18} between the labelled fluorides and fluoride deposits on the surface of the chamber which was necessarily exposed to the gas. Besides this, a small loss of the sample was always observed. Due to these factors the reliability of determinations was believed to be limited to ± 4 per cent.

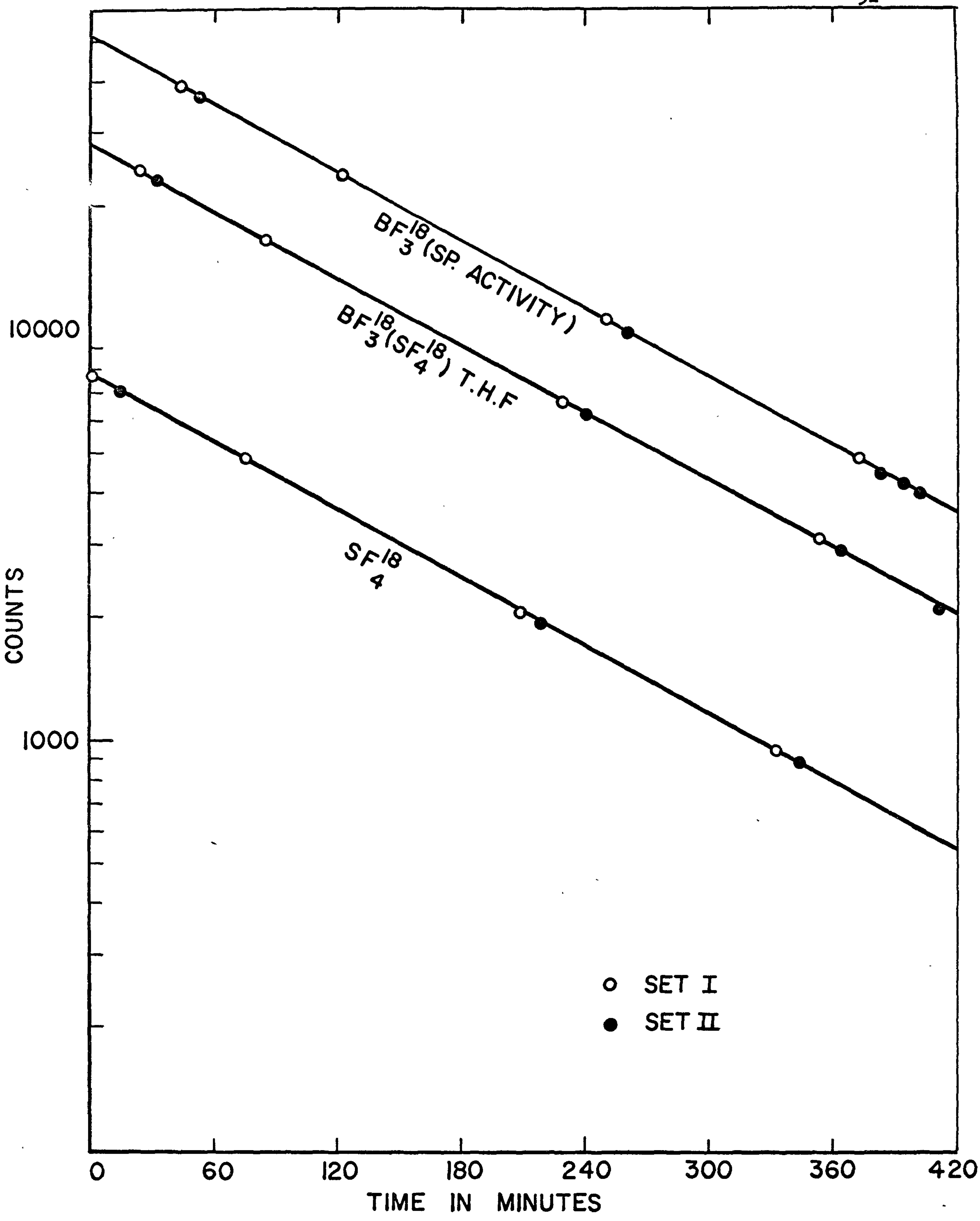
Bernstein and Katz96,112) improved upon this technique by computing the activities on the basis of pressure rather than weights of the gaseous fluorides. Adam, Bernstein and Katz96,113) used a nickel chamber in order to reduce the background ascribed to the heterogeneous exchange with the surface. In all these measurements half-lives of 112 ± 1 minutes96) were obtained consistently.

In counting fluorine-18 the errors due to self-absorption, back-scattering, self-scattering, absorption by the detector window, etc. are negligible96,97) because the annihilation γ-rays from F^{18} are monoenergetic and they have considerable energy. Thus the counting of fluorine-18 is much simpler than for many isotopes.

In the present work fluorine-18 has been counted in aqueous solution. It was assayed in a known volume by scintillation spectrometry using the counting equipment described above. In order to check the reproducibility of the counting method samples for counting F^{18} were made as follows. From each solution containing fluorine-18 duplicate, 5 $m\ell$ portions were placed in dry 20 $m\ell$ test tubes, by means of a 5 mℓ pipette coupled to a hypodermic syringe. These samples were then counted in the well type scintillation counter at 0.511 Mev. Each sample was counted for ten minutes and the counting was repeated several times over a period of three half-lives of fluorine-18. The actual time of each reading was recorded. The count rate of each sample after deducting the average background was plotted against time on semi-log graph paper. The graphs gave the expected value for the half-life of fluorine-18, i.e. 109 ± 1 minutes and the graphs for the duplicate samples agreed well (Fig.5), showing that the counting technique was accurate and reproducible. From these graphs the activity of F^{18} can be obtained at any arbitrary time.

The relative activity of the labelled compounds, as reported in this work, was calculated from the number of counts per minute measured according to the procedure described above. The count rate depended upon the efficiency of the detector, geometry of counting, dead time of the system and channel width of the discriminator. As it was not necessary to do absolute counting all relative measurements were obtained with fixed analyser settings, after calibration of these with the Cs^{137} standard.

The foregoing procedure for counting fluorine-18 does not need any elaborate equipment or stringent precautions and is much faster than the methods employed by Knight, Katz and Bernstein, etc. In a relatively short time several samples containing F^{18} can be counted with the same equipment under identical conditions.



DECAY CURVES OF LABELLED BF_3 and SF_4

FIG: 5

Applications of Fluorine-18

It is somewhat surprising that only a few investigators have made use of this isotope, which has been known for such a long time. Dodgen and Libby111) appear to have been the first to use fluorine-18 in chemical exchange studies. They were concerned with the general problem of halogen exchange in the gas phase, between halogen acids and the corresponding halogens. They did not observe any exchange between hydrofluoric acid gas and fluorine at room temperature and, therefore, they considered that an intermediate complex was not formed.

Fluorine-18 exchange between hydrogen fluoride and the halogen fluorides $C\ell F_3$, BrF_5, $1F_5$ and $1F_7$ has also been studied13,96,110). Halogen fluorides are thought to participate in ionic equilibria of the type

$$C\ell F_3 + HF \longrightarrow C\ell F_2^+ + HF_2^-$$

$$BrF_5 + HF \longrightarrow BrF_4^+ + HF_2^-$$

If these equilibria do in fact exist in mixtures of hydrogen fluoride and halogen fluorides, then exchange of fluorine-18 should occur with great ease via the common ions. It was observed by Rogers and Katz96,110) that HF^{18} exchange fluorine completely in ten minutes or less with BrF_3, $C\ell F_3$, BrF_5 and IF_5.

In the gas phase13,96,110) it was found that HF^{18} exchanges fluorine rapidly with $C\ell F_3$, BrF_3, BrF_5 and $1F_7$ at room temperature. It could not be determined whether these exchanges are homogeneous or heterogeneous reactions. Similarly $C\ell F_3^{18}$ and BrF_3 were found to exchange very rapidly in the gas phase. With fluorine compounds in which the bonds are predominantly of covalent character such as SF_6 or $CC\ell_2F_2$ no exchange was observed with HF^{18} at room temperature13).

The gas phase isotopic exchange reactions of fluorine with labelled $C\ell F_3$, BrF_5 and IF_7 were studied by Bernstein and Katz13,96,112). Practically no exchange was observed at room temperature, however, equilibrium was attained at 300°. Measurable rates were observed between 120° and 250°.

From thermodynamic data for the reaction

$$C\ell F_3 \longrightarrow C\ell F + F_2$$

and the dissociation pressures of IF_7 and BrF_5 Bernstein and Katz13,112) concluded that reversible dissociations would account for the exchange observed with $C\ell F_3$ and IF_7. Bromine pentafluoride was, however, found to be very stable with less than 0.1 per cent dissociation, at 400°. Consequently dissociation could not account for the exchange and an associative mechanism or complex formation between fluorine and BrF_5 was suggested. However, no definite evidence could be found for the suggested mechanism.

A quantitative study of the kinetics of these exchange reactions was later carried out by Adams, et al.13,113). They found that the rate of the exchange reaction was a linear function of the concentration of fluorine, and a complex function of the concentration of the halogen fluoride. The work was done in a nickel container in the temperature range 181° to 257°. A large amount of kinetic data was obtained for the reactions

$$F_2 + C\ell F_3^{18} \longrightarrow F_2^{18} + C\ell F_3$$

$$F_2 + BrF_5^{18} \longrightarrow F_2^{18} + BrF_5$$

$$F_2 + IF_7^{18} \longrightarrow F_2^{18} + IF_7$$

The concentration dependence of the exchange reaction rate showed a maximum with all the halogen fluorides, however, it was most pronounced in the $BrF_5 - F_2$ system. On the basis of their observations the authors concluded that $C\ell F_3 - F_2$ and $IF_7 - F_2$ exchange occurred by combined heterogeneous and homogeneous mechanisms involving dissociation of the halogen fluoride, while the $BrF_5 - F_2$ exchange took place through a heterogeneous mechanism only.

The exchange reactions of the three halogen fluorides with $A\ell F_3$, NiF_2, CuF_2 and CaF_2 have also been studied briefly13). Exchange of F^{18} was observed, but it was not fast enough to account for the rate of exchange between the halogen fluorides and fluorine.

In 1955 Adam, et al.13,114) found fluoride to be an active catalyst for the following gas phase reactions

$$HF^{18} + F_2 \longrightarrow HF + F_2^{18}$$

Data were obtained over a wide range of concentrations at 467°, 497° and 530°K. It was concluded that the reaction proceeds by a heterogeneous catalysis mechanism.

Complex fluorides have received little attention. It has been found that aqueous solutions of fluoride ion labelled with fluorine-18 undergo complete exchange with inactive H_2SiF_6 in aqueous solution at a pH 0.5 to 1.0 after standing for five minutes at room temperature[13,115)]. Studies have also been made which involve exchange of fluorine atoms between alkali fluorides and silicon tetrafluoride[13,72)]. The four alkali fluorides used were LiF^{18}, KF^{18}, RbF^{18} and CsF^{18}. Manometric measurements showed that the systems KF - SiF_4, RbF - SiF_4, CsF - SiF_4 underwent compound formation as well as exchange [13,72)] The system LiF - SiF_4 showed no evidence of compound formation, however, a large amount of exchange was observed[72)]. The authors neither suggest the mechanism of exchange nor give any explanation for the difference in behaviour of LiF and the other alkali fluorides. It is suggested that fluorine-18 exchange, in the system LiF-SiF_4 takes place via an unstable intermediate Li_2SiF_6. The instability of Li_2SiF_6 is due to the small size and high polarizing power of Li^+ and the relatively weak acceptor strength of SiF_4. In the case of SiF_4 the amount F^{18} exchanged under similar conditions was less than for BF_3 (Chapter 3) which also suggests that Li_2SiF_6 is less stable than $LiBF_4$.

The interactions of gaseous and solid fluorine containing compounds has been summarised by Bernstein and Katz[13,96)] (Table 5). The results have only a qualitative significance.

A system of particular interest because of its theoretical importance and practical application is the NaF - UF_6 system. Sodium fluoride has been used for many years to purify UF_6[97)]. Martin and

TABLE 5[13,96)

Fluorine-18 Exchange Between Gaseous and Solid Fluorides at Room Temperature

	NaF	LiF	$NaHF_2$	CaF_2	CuF_2	NiF_2	$A\ell F_3$
HF	+++	+++	+++	+	+	+	+
F_2	-	-	-	-	-	-	-
$C\ell F_3$	++	+++	+++	+	+	+	+
BrF_5	++	+++	++	+	+	+	+
IF_7	++	+++	++	+	+	+	+

+++	Rapid and complete exchange with bulk solid.
++	Slow exchange with bulk solid.
+	Exchange with only surface layers of solid.
-	Negligibly slow or no exchange.

Albers[97,116)] reported the formation of stable complexes between UF_6 and NaF and some other inorganic fluorides. The formula proposed for the sodium complex was $3NaF.UF_6$. In order to determine whether the sodium complex is a compound with expanded U-F lattice or merely involves the absorption of UF_6 on the NaF surface, a study of F^{18} exchange between UF_6 and NaF was undertaken[97)]. The complex labelled with F^{18} was made by condensing UF_6 on NaF^{18} [97)]. It was decomposed by heating and the fraction of F^{18} in both the reactants, NaF and UF_6, was determined. The results of the experiment indicate that there is a substantial amount of exchange between NaF^{18} and gaseous UF_6, at a temperature where the solid complex has high dissociation pressure. Thus in the solid complex UF_6 is not merely absorbed on the surface of NaF. However, the fraction of F^{18} exchanged was not as large as expected for the proposed formula i.e. $3NaF.UF_6$. If this formula were correct about 65 per cent. of F^{18} should be transferred to UF_6. The authors do not give any detailed results in their communication[97)], however, they state that "the results appear to indicate that either not all the fluorine atoms are exchanged or that there may be more than one stable complexes between UF_6 and NaF.

Frank and Foster[117)] have made an extensive study of the processes involved in the preparation of aluminium by electrolysis of Na_3AlF_6 - Al_2O_3 melt. From fluorine-18 exchange studies they concluded that fluoride ion was not present in the melt.

It has been reported that compounds such as CH_2F_2, CHF_3, CH_3F and CF_4 do not exchange fluorine atoms with HF^{18}, even after heating for one hour at temperatures ranging up to 500° [13,118)].

Higher temperature measurements could not be used because of chemical decomposition.

Exchange reactions between various fluorocarbons and metallic fluorides in the temperature range 30° to 250° were studied by Gens, et al.13,119). All the alkali fluorides were found to exchange readily with fluorocarbons, however, the order of reactivity per square meter of the surface area was found to be $Cs > Rb > K \sim Na \sim Li$. Any single salt exchanged more readily with C_3F_6 than with CF_4, C_4F_{10} and $(C_2F_5)_2O$, although appreciable exchange was observed in all cases. No attempt was made to establish the kinetics of the reaction. These investigators also showed that SF_6 does not exchange fluorine with any of these salts below 300° and above that temperature, complicated side reactions vitiated the results.

An additional study of exchange reactions of fluorocarbons with a number of metallic fluorides was reported in a later paper13,120). All alkali fluorides exchanged more readily than did a number of other salts.

Gens and Wethington13) have also made some kinetic studies of the reaction between CsF and C_3F_6 at 0° and 55°. A large amount of exchange occurred as soon as the gas was placed in contact with the solid. The fast reaction was then followed by a slow zero order reaction. The catalytic oxidation of C_3F_6 was studied using NaF and CsF13,121). The catalytic activity of the fluorides and selectivity in the products of oxidation was found to be temperature dependent, as expected for the extreme members of the family. For example, C_3F_6 could be oxidised in the presence of CsF at 215°, but NaF was ineffective at that temperature; the products of the catalytic oxidation of C_3F_6 by CsF contained 20 per cent perfluorylacetone, while in the case of NaF catalyst the yield was 1 per cent at 300°.

Fluorobenzene saturated with HF has been irradiated with fast neutrons to study the chemical effects of F^{19} (n,2n) F^{18} reaction[13,122). After irradiation it was found that 0.64 per cent of the total activity could be extracted with aqueous phase, but the nature of F^{18} in organic phase was not determined.

In addition to the above mentioned application fluorine-18 has been employed in the investigation of tooth decay[13, 123) and the distribution of fluorine in bone etc.[13,124).

CHAPTER 3

Preparation of F^{18} Labelled Covalent Fluorides

In this chapter the preparation of BF_3^{18}, SF_4^{18}, AsF_5^{18}, PF_5^{18}, SiF_4^{18} and SeF_4^{18} are described. Only the labelled SiF_4 has previously been reported72). It was made by circulating SiF_4 over LiF^{18} prepared by F^{19} (p,pn) F^{18} reaction95). In the present investigation essentially the same method has been used for labelling BF_3, SF_4, PF_5, AsF_5, SiF_4 and SeF_4.

In the case of BF_3 it was not necessary to separate the LiF^{18} from the large excess of Li_2CO_3 irradiated with thermal neutrons.

The following factors were considered essential when selecting suitable procedure for labelling the gases:-

1. The method should be rapid.
2. It should be capable of giving a product of high radio chemical purity.
3. The specific activity of the compound should be at least 10^4 cpm per gram.
4. The apparatus should be as simple as possible.

In order to check the radiochemical purity of the labelled product it was absorbed in 20mℓ of 4N Na OH, the solution was diluted to 250 mℓ and F^{18} was counted as described in Chapter 2. In every case the half-life of radioactive species was found to be 109 ± 1 minutes.

The decay curve did not show any tail after about eight half-lives of F^{18}, indicating no significant radioactive impurity contributing to the counting measurements.

Preparation of BF_3^{18}

When lithium carbonate is heated with BF_3 in a closed vessel at 300° for a few hours $LiFB_4$ is formed according to the following equation35)

$$3Li_2CO_3 + 9BF_3 = (BOF)_3 + 6LiBF_4 + 3CO_2$$

Since the dissociation pressure of $LiBF_4$ is one atmosphere at 322° 35) labelled BF_3 can be prepared by passing boron trifluoride over heated LiF^{18} by utilizing the equilibria

$$LiF^{18} + BF_3 \longrightarrow LiBF_3F^{18} \longrightarrow BF_3^{18} + LiF.$$

As mentioned in Chapter 2 fluorine-18 is present as fluoride in the irradiated lithium carbonate. Thus there seemed to be a strong possibility that LiF^{18} would exchange F^{18} with BF_3, via the intermediate $LiBF_4^{18}$.

Procedure

For the preparation of F^{18} a 100 mg. sample of pure dry lithium carbonate was irradiated with thermal neutrons as described in Chapter 2. After a 'cooling' period of thirty minutes the lithium carbonate was transferred to a pyrex glass boat and it was placed in the reaction tube R (Fig.6). The tube was heated to 200° while the whole apparatus was flushed with a rapid current of purified nitrogen for five to ten minutes. Then a slow stream of BF_3 was passed through the reaction tube while the temperature was maintained at 200°. The resulting gases were passed through the traps A, B and C. The traps A and B were cooled in a freezing mixture of dry ice and chloroform in order to collect the boron oxyfluoride trimer. Initially C was at room temperature and for about ten minutes BF_3 containing tritium and CO_2 was allowed to escape into the laboratory exhaust. Then the receiver C was cooled in liquid air to condense BF_3^{18} and the temperature of the reaction tube was raised to 320°. After about forty-five minutes 3 to 4 grams of BF_3^{18} had accumulated which had a count rate of the order of 10^5 cpm/g. BF_3. The specific activity of BF_3^{18} could be increased by decreasing the rate of flow of boron trifluoride and vice versa. The condensed BF_3 would not be expected to have a uniform isotopic distribution of F^{18} and it was, therefore, evaporated at -100° into the previously evacuated and dried storage flask F (Fig.6).

The radiochemical purity of the product was checked by determining the half-life of the radioactive species.

Preparation of LiF^{18}

In the preparation of labelled SF_4, SiF_4 and PF_5 etc. labelled lithium fluoride was required. This was prepared by producing

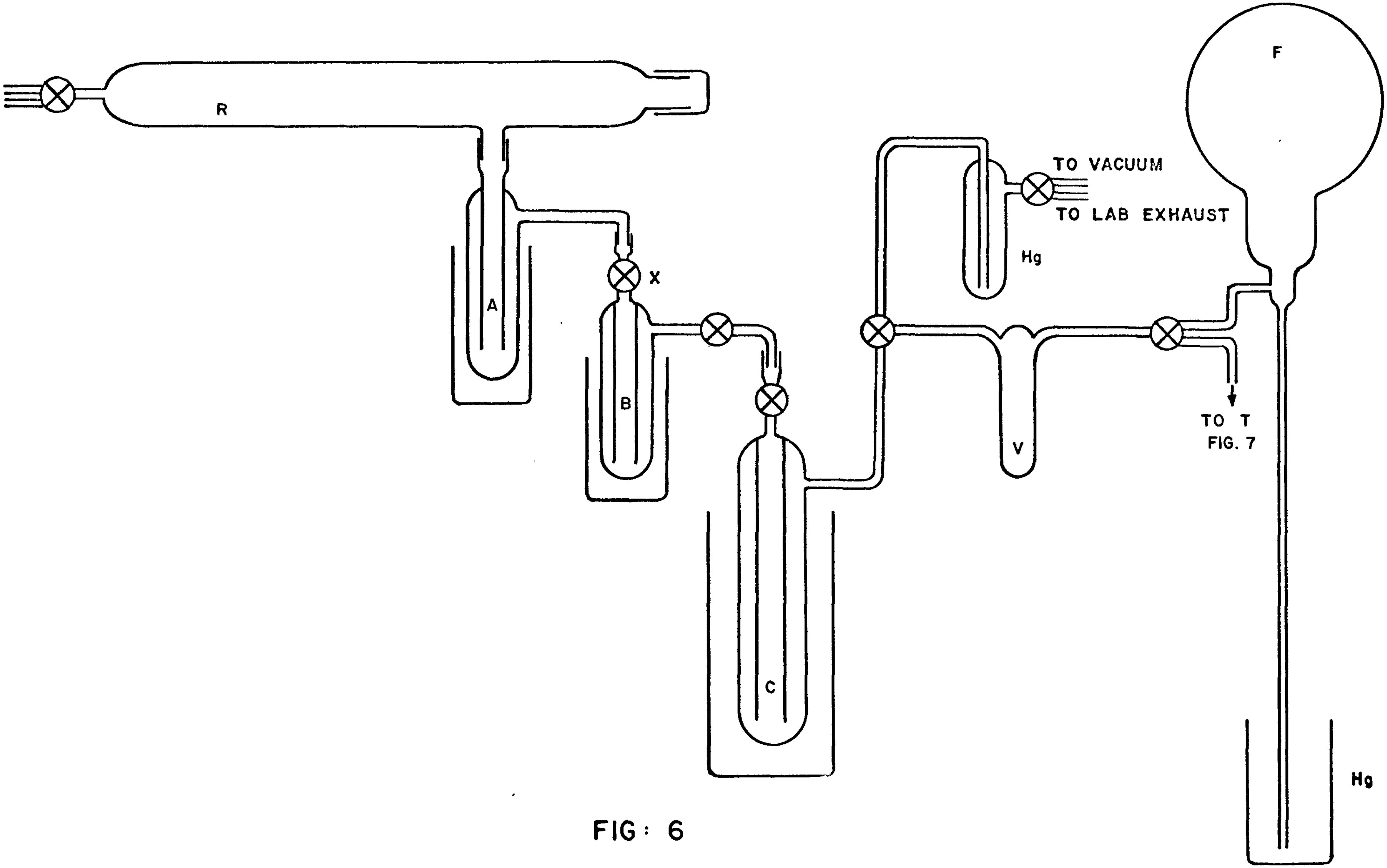


FIG: 6

F^{18} and converting this to LiF^{18}. In 1963 Felix, et al.125) reported a procedure for the separation of F^{18}. These authors irradiated eight grams of lithium nitrate with an integrated thermal neutron flux of 7 x 10^{15} cm^{-2}. After irradiation BaF_2^{18} was coprecipitated with $BaSO_4$ from 50 mℓ solution with 8.5 mℓ of 0.1N $(NH_4)_2\ SO_4$ and 9 mℓ of 0.1N $Ba(NO_3)_2$. From the solid product HF^{18} was obtained by adding CaF_2 and H_2SO_4. The total fluorine-18 produced was 2.9 - 4 μc/g. of lithium nitrate and 45-48 per cent. of F^{18} was coprecipitated.

The preparation of LiF^{18} by the foregoing procedure is cumbersome and time consuming and the product would not have the high specific activity which was desired in the present investigation. In view of the relatively short half life of fluorine-18 and the nature of the contemplated study it was necessary to develop an alternative procedure for the separation of fluorine-18.

In 1959 Caley and Kahle126) reported that lithium fluoride is quantitatively precipitated in 50 per cent. ethanol solution. They used this property for the quantitative determination of fluoride ion. This procedure was, therefore, modified to prepare LiF^{18} from the irradiated lithium carbonate.

Procedure

A 100 mg sample of the irradiated lithium carbonate was placed in a 250 mℓ polyethylene beaker which contained 100 mg of Li_2CO_3. The lithium carbonate was made into a slurry with distilled water and dilute hydrofluoric acid (5 per cent.) was added drop by drop until it just dissolved all the carbonate. Alcohol was then added until the aqueous phase had 50 per cent alcohol by volume. The labelled lithium fluoride was separated by centrifuging. It was then washed three times with 50 per cent ethanol solution, three times with absolute ethanol, three times with dry ether and dried at 200° for one hour.

The half-life of fluorine-18 in the product was found to be 109 ± 1 minutes and there was no detectable radiochemical impurity. The total amount of F^{18} produced was about 8.9 μc. The yield of fluorine-18 was 90 per cent. The entire operation was completed in just under two hours after the irradiation.

This procedure has several advantages over the one developed by Felix, et al.125). It is much faster and the yield of F^{18} is higher by an order of two magnitudes. The radiochemical purity of F^{18} is at least as high as that obtained by the former procedure. Fluorine-18 is separated as LiF^{18} and no additional carrier is necessary for the regeneration of HF^{18}. If it were not necessary to dry the LiF^{18} the separation of LiF^{18} could be completed in about one hour after the irradiation of lithium carbonate.

Preparation of SiF_4^{18}, SF_4^{18}, PF_5^{18} and AsF_5^{18}

The gases were labelled by passing them over LiF^{18} at high temperature using the apparatus employed in the preparation of BF_3^{18} (Fig.6).

It is suggested that SiF_4 reacts with LiF_4^{18} through an unstable intermediate Li_2SiF_6 although there is no evidence for its existence even at low temperature71,72).

In 1963 Tunder and Seigel[22)] provided positive evidence for the existence of the SF_5 anion as $(CH_3)_4NSF_5$, which is stable at ambient temperature. Therefore, the mechanism of exchange between SF_4 and LiF^{18} may be represented by the following equation

$$LiF^{18} + SF_4 \longrightarrow LiSF_5^{18} \longrightarrow LiF + SF_4^{18}$$

The intermediate $LiSF_5$ would be expected to be less stable than Li_2SiF_6 because SF_4 is a weaker acceptor than SiF_4. The reason for the instability of $LiSF_5$ is the same as that for Li_2SiF_6 (Chapter 2).

Similarly the exchange reactions of AsF_5 and PF_5 may proceed through the MF_6^- (M = As or P) ion. Both of these compounds have been shown to form complexes of the type AMF_6 [9,13,53,127)].

Procedure

The dry LiF^{18} was transferred to a pyrex glass boat and it was placed in the reaction tube R (Fig.6). The tube was heated to 150° while the whole apparatus was flushed with a rapid current of purified nitrogen for five to ten minutes. Then a slow stream of the desired gas was passed through the reaction tube and the temperature was raised to about 200°. The gases coming out of the reaction tube were passed through the traps A, B and C. Traps A and B were cooled to about -30° in a carbon tetrachloride bath and C was cooled in liquid air to condense the labelled fluoride. After about forty to forty-five minutes when enough labelled compound had been collected the flow of the gas was stopped. The stop cock X was closed and C and V were evacuated. The labelled gas was warmed and vacuum distilled at low temperature (SF_4 at -100°, SiF_4 at -95°, AsF_5 and PF_5 at -70°) into the receiver V cooled by liquid air. It was then evaporated into the storage flask F in order to ensure uniform isotopic distribution.

The count rate of these gases determined six hours after the irradiation of Li_2CO_3, varied between 2×10^4 to 2.5×10^5 cpm per gram of the gas. The specific activity in every case could be increased or decreased by adjusting the rate of flow of the gas.

Sulphur tetrafluoride was also labelled by liquid-solid phase exchange reaction, i.e. by reacting liquid SF_4 with dry LiF^{18}. The mechanism of the reaction is presumed to be the same as in the preceeding method.

The dry LiF^{18} was placed in the reaction vessel D (Fig.7). The apparatus (Fig.7) was connected to the vacuum line (Fig.8) and evacuated. The stop cocks 1 and 4 (Fig.8) were closed and the evacuated bulb C (Fig.8), measuring about 500 mℓ, was filled with SF_4 at atmospheric pressure. The stop cocks 3 (Fig.8) and 2 (Fig.7) were closed and the reaction vessel was cooled in liquid air. Thereafter the stop cock 1 (Fig.9) was opened and the SF_4 was condensed on top of the LiF^{18}. Then the stop cock 1 (Fig.7) was closed and the contents of the reaction tube were warmed to -40° and kept at this temperature for thirty minutes. Then the stop cock 2 (Fig.7) was opened and $SF_4{}^{18}$ was distilled into the receiver E (Fig.7) cooled in liquid air.

The specific activity of $SF_4{}^{18}$ was much less than that of $SF_4{}^{18}$ obtained by gas - solid phase exchange reactions.

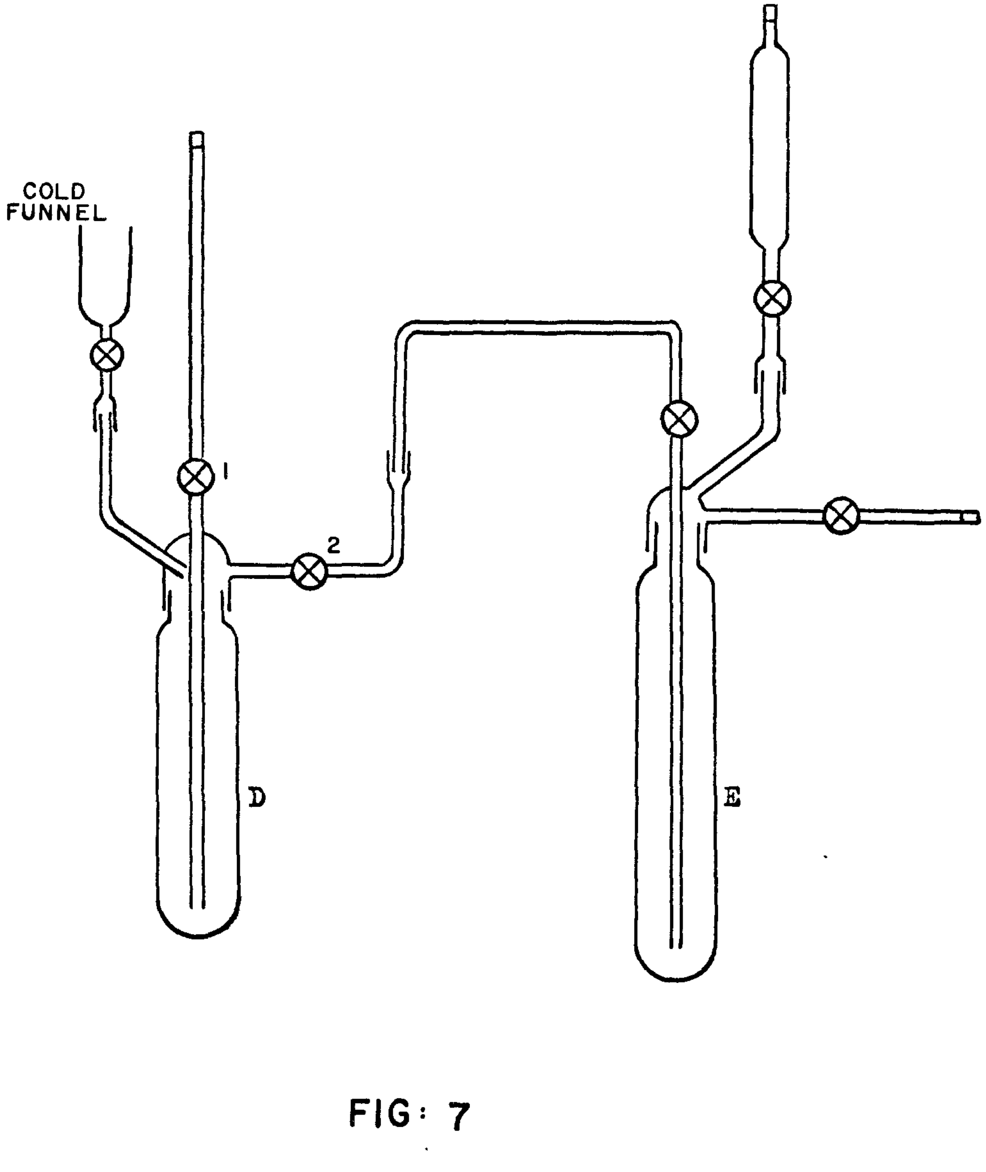


FIG: 7

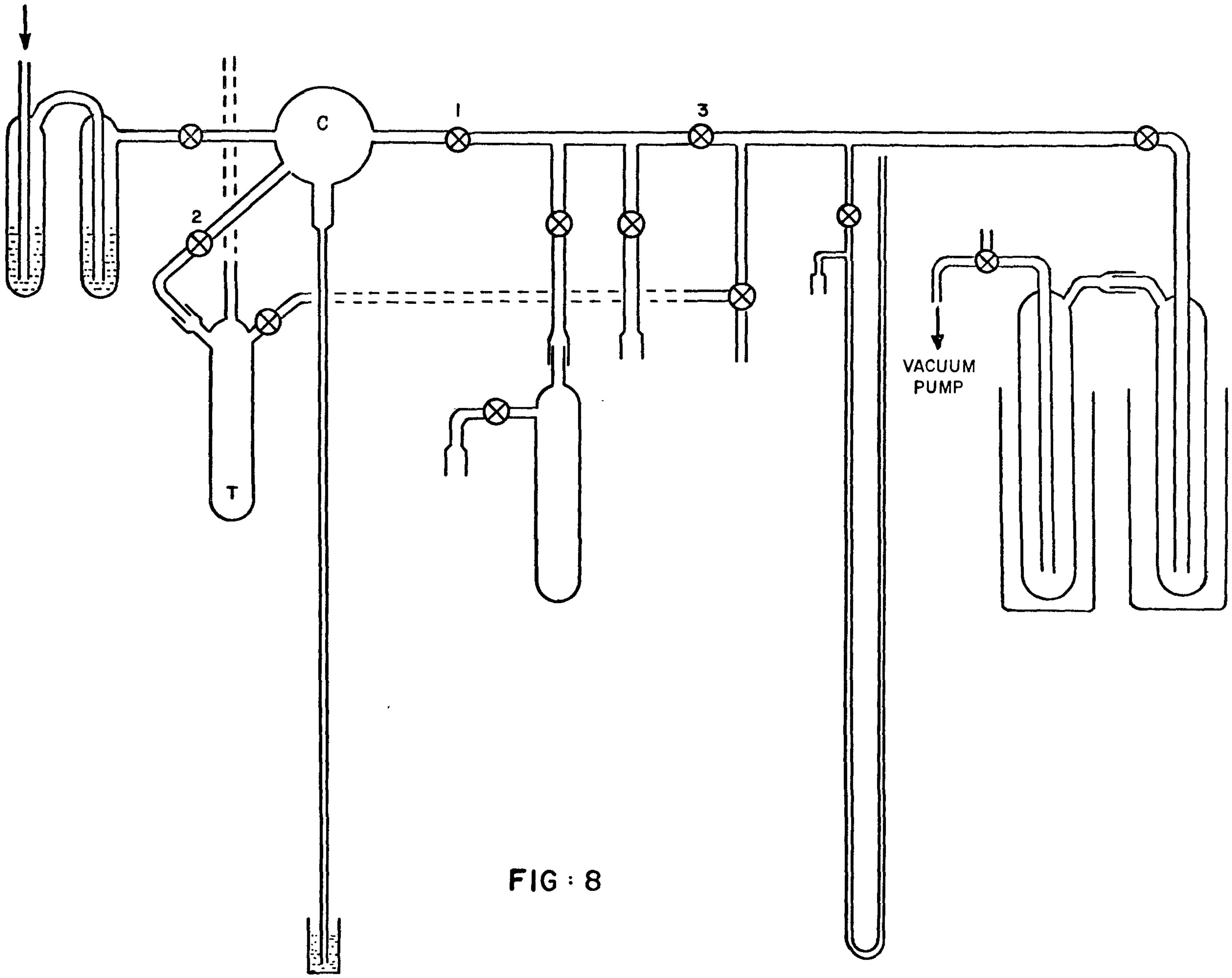


FIG : 8

Preparation of Labelled SeF_4

Selenium tetrafluoride was labelled by a liquid-solid exchange reaction. It is known the SeF_4 forms complexes involving the ion SeF_5^- 14). Therefore, the mechanism of exchange is assumed to involve the following reaction

$$LiF^{18} + SeF_4 \longrightarrow LiSeF_5^{18} \longrightarrow LiF + SeF_4^{18}$$

Procedure

The dried LiF^{18} was placed in the reaction vessel D (Fig.7) to which the tube containing SeF_4 was joined by means of a ground glass joint in place of the 'cold funnel', and the apparatus was connected to the vacuum line. Then the stop cocks 1 and 2 (Fig.7) were closed and the reaction vessel was cooled in liquid air. The glass seal on the SeF_4 tube was broken and the SeF_4 was distilled under vacuum into the reaction vessel D (Fig.7). The contents of the reaction vessel were warmed to room temperature and after thirty minutes the selenium tetrafluoride was distilled under vacuum into the receiver E (Fig.7). The condensate was hydrolysed with an excess of 10 per cent. NaOH to determine its specific activity and the half life of the radio - active species. The observed count rate was found to be of the order of 10^4 cpm/g. SeF_4 and the half-life of the radio-isotope agreed with that of F^{18}.

CHAPTER 4

Analytical Methods

In every case the covalent fluoride was hydrolysed in order to convert it into its corresponding oxyacid, which was then determined by a standard or suitably modified procedure. From the amount of oxyacid or its salt the quantity of the corresponding gaseous fluoride was calculated.

Determination of SF_4

When a Lewis base such as diethyl ether, tetrahydrofuran (THF) or dimethyl formamide (DMF) is added to an SF_4 - Lewis acid complex, the Lewis acid forms a stable complex with the Lewis base and the SF_4 is liberated[23-25)]. The SF_4 is separated from the mixture by distillation under vacuum. The SF_4 distilled over, usually contains a small amount of either ether or tetrahydrofuran. However, part of the SF_4 remains dissolved in the excess of the Lewis base and is mixed with either BF_3, AsF_5, PF_5 or SiF_4. When excess NaOH solution is added to these fractions the constituent fluorides are hydrolysed to the sodium salts of their corresponding oxyacids, viz: SF_4 to Na_2SO_3, BF_3 to Na_3BO_3, PF_5 to Na_3PO_4 and the concomittant sodium fluoride. The complexes $AsF_5.(C_2H_5)_2O$ and $SiF_4.(DMF)_2$ do not appear to undergo the expected hydrolytic reaction. This will be discussed later. The Na_2SO_3 present in the solution either alone or with oxyacids of B, P or As was oxidised with H_2O_2 in alkaline medium and barium sulphate precipitated[128,129)] by adding a dilute solution of $BaCl_2$ to the hot solution acidified with HCl. The precipitate was filtered off, washed with hot water, carefully ignited at red heat and weighed as $BaSO_4$. The amount of SF_4 was calculated from the weight of barium sulphate.

For the determination of sulphate in the presence of soluble silicates the logical procedure would be to separate silica in the first step and then precipitate $BaSO_4$ from the filtrate and the washings. Consequently as a first step for the separation of SiO_2 from the test solution containing SO_3^{2-}, dimethyl formamide, NaF and presumably Na_2SiO_3, it was oxidised with H_2O_2 in alkaline medium, treated with 2 per cent $HClO_4$ saturated with boric acid and then evaporated to dense white fumes[128)]. After cooling the contents were diluted with water. Surprisingly, the yield of SiO_2 was not more than 10 per cent of the theoretical value. An alternative procedure for the determination of SiO_3^{2-} in the presence of F^- using $(NH_4)_2CO_3$ was employed[128)]. On adding excess of $(NH_4)_2CO_3$ or NH_4Cl to the cold solution a thick gelateneous precipitate was thrown down, most of which redissolved on heating. An aliquot of the test solution was then acidified with hydrochloric acid and boiled vigorously for ten minutes, but there was not even the slightest turbidity. The solution was then evaporated to about 1/4 of its volume and then diluted. Remarkably the solution was crystal clear.

The above observations strongly suggested the possibility of using the test solution directly for the precipitation of $BaSO_4$. However, before commencing the determination of SO_4^{2-} a few qualitative observations were made to ascertain that the soluble silicon compound would not interfere with the precipitation of $BaSO_4$. To about 25 mℓ of the test solution hydrogen peroxide was added to oxidise SO_3^{2-}. The solution was boiled to decompose excess H_2O_2. It was then diluted to about 350 mℓ and acidified with HCℓ. The acidified solution was boiled for one hour and then kept over a steam bath for forty-eight hours. At the end of the period the solution was clear and colourless.

In the light of the foregoing observations it is very doubtful that in the test solution silicon is present as SiO_3^{2-}. It is probably present as a complex of either silicic acid or SiF_4 with dimethyl formamide or F^- and the complex is not decomposed by acids. In order to investigate whether DMF is the complexing agent or the fluoride ion the following experiments were done. About 2 mℓ of dimethyl formamide were added to about 25 mℓ of 0.2N Na_2SiO_3 solution. On boiling the acidified solution $SiO_2 \cdot x\ H_2O$ was precipitated, but it redissolved on adding considerable excess of DMF, about 10-15 mℓ. This observation suggested that dimethyl formamide is the main complexing agent. Presumably the complex is of the type $Si(OH)_4.(DMF)_x$ (x = 1 or 2) analogous to $SiF_4.(DMF)_x$ 67).

Determination of SO_4^{2-} in the presence of SiO_3^{2-} and F^-.

As a result of the above observations barium sulphate was directly precipitated in the presence of DMF from an acidic solution containing SO_4^{2-}, F^- and SiO_3^{2-}. To ascertain the reliability of this method a standard solution of Na_2SO_3 containing sodium silicate, sodium fluoride, was made. To a 25 mℓ portion of the simulated solution 1-2 mℓ of DMF were added followed by 2 mℓ of 30 per cent H_2O_2 to oxidise SO_3^{2-}. The solution was then boiled to decompose excess H_2O_2, diluted to 250 mℓ and acidified strongly with HCℓ. The solution was heated to boiling and an excess of 5 per cent $BaC\ell_2$ solution was added slowly with constant stirring. The solution was kept over a steam bath for a few hours to granulate the precipitate. The clear solution was decanted through a Whatman No. 42 filter paper. The precipitate was washed, transferred to the filter paper and then ignited in a weighed silica crucible to a constant weight, according to the recommended procedure128,129). The results are given in Table 6.

Determination of SF_4 in the system SF_4-SiF_4

In the investigation relating to the exchange of F^{18} between SiF_4^{18} and SF_4, sulphur tetrafluoride was separated by adding a 2:1 mixture of ether and dimethyl formamide at about -60°, silicon tetrafluoride formed a 1:2 complex with DMF and the SF_4, set free, was collected in a receiver cooled in liquid air. However, at this low temperature some of the SF_4 remained dissolved in the ether - DMF mixture.

In a separate experiment it was observed that $SiF_4 \cdot (DMF)_2$ does not fume in moist air and dissolved in water without any apparent decomposition yielding a transparent solution which remained clear

TABLE 6

Weight of Na_2SO_3 in 25 mℓ of the solution containing SiO_3^{2-}	Calculated weight of $BaSO_4$ from 25 mℓ of the solution	Weight of $BaSO_4$ in 25 mℓ of the solution found.
0.1637 g.	0.3031 g.	0.3042 g.
"	"	0.3047 g.
"	"	0.3029 g.

even after adding excess of aqueous NaOH. If the order of addition of water and alkali is reversed a turbid solution is obtained. The turbidity slowly disappeared after adding a large excess of dimethyl formamide. Therefore, first ice-cold water was added to the mixture containing $SiF_4.(DMF)_2$, DMF, SF_4 and ether. followed by an excess of ice-cold solution of sodium hydroxide. The resulting solution was heated in a steam bath to volatalize most of the ether. After cooling to room temperature it was made up to 250 mℓ, and 25 mℓ aliquots were used for the determination of SF_4 via $BaSO_4$ employing the above mentioned procedure. However, in this case an additional quantity of DMF was not necessary.

Determination of SF_4 in the absence of SiF_4

The solution obtained by hydrolysing SF_4 either alone or with BF_3, PF_5 or AsF_5 was heated on a steam bath to evaporate ether if present in excess. After cooling the solution was made up to 250 mℓ. For the determination of $BaSO_4$ 25 mℓ portions of these solutions were used. Barium sulphate was determined according to the recommended procedure[128,129].

Determination of BF_3

The determination of BF_3 for the specific activity measurement was fairly straightforward. An approximately known volume of BF_3^{18} was absorbed in NaOH (Chapter 5). The boric acid content of the solution was determined by titration in the presence of mannitol[130)]. The quantity of BF_3 was then calculated from the amount of H_3BO_3.

A 25 mℓ aliquot of the solution was taken in a 350 mℓ conical flask. The solution was neutralized to the methyl red end point and 25 mℓ of 20 per cent $CaCl_2$ solution was added. The solution was then titrated in the cold with 0.3N NaOH to the methyl red end point and then boiled under reflux for one hour. After cooling the solution was titrated to the same end point and one mℓ of the standard solution was added in excess and the refluxing continued for three hours. The solution was cooled to room temperature and then back titrated to the first appearance of red colour with 0.3N HCℓ. Then the solution was diluted to about 150 mℓ with freshly boiled distilled water. Nitrogen was bubbled through the solution for ten minutes to remove CO_2, then 5-6 gms of mannitol, and six drops of 0.1 per cent phenolphthalein solution were added. The solution was then titrated with 0.1 N NaOH to the end point of phenolphthalein. From the volume of decinormal sodium hydroxide solution used in the titration the amount of BF_3 was calculated.

Determination of BF_3 in the presence of SF_4 and THF

The estimation of BF_3 in the solution obtained by decomposing the $SF_4{\cdot}BF_3$ adduct with THF could not be carried out according to the above procedure, because one of the products of hydrolysis, viz: Na_2SO_3, a salt of a weak acid, interferes with the determination. Therefore, Na_2SO_3 was first oxidised to SO_4^{2-} in alkaline medium with

2 mℓ of 30 per cent H_2O_2. When H_3BO_3 was determined by the foregoing method very high values were obtained, presumably for the following reason. The complex BF_3·THF when hydrolysed yields Na_3BO_3, NaF and THF, but it is quite possible that simultaneously, or later, some THF undergoes ring opening producing the corresponding dihydric alcohol[131)]. When hydrogen peroxide is added to the solution, sulphite is oxidised to sulphate and the dihydric alcohol to the corresponding carboxylic acid. The carboxylic acid, would result in higher values for H_3BO_3. In order to check this assumption the following experiments were performed. To a solution containing a known amount of boric acid some sodium sulphite and NaF were added. The sulphite was oxidised by 30 per cent H_2O_2 and H_3BO_3 was determined volumetrically in the presence of mannitol. The amount of H_3BO_3 determined agreed with the actual value. In another experiment Na_2SO_3, NaF and tetrahydrofuran were added to a solution of boric acid of known strength. The alkaline solution was boiled almost to dryness in order to expel tetrahydrofuran. The residue was dissolved in about 20 mℓ of water and SO_3^{2-} was oxidised with mℓ of 30 per cent H_2O_2. After decomposing the excess of H_2O_2 boric acid was determined as before. A high value for boric acid was obtained confirming the above suggestion concerning tetrahydrofuran. Therefore, a modified method for the estimation of BF_3 in such a solution was worked out and checked as follows.

A standard solution of boric acid was made which contained tetrahydrofuran, Na_2SO_3 and NaF.A 25 mℓ portion of the simulated solution was boiled to expel as much tetrahydrofuran (THF) as possible.

After cooling, 30 mℓ of 1 per cent H_2O_2 wereadded to oxidise SO_3^{2-} and the solution was boiled until the excess of H_2O_2 was completely decomposed. The solution was then treated for the determination of H_3BO_3 as described in the preceding method. The results were reproducible and are given in Table 7.

The test solution of BF_3 and SF_4 in THF was hydrolysed with excess of NaOH and made up to a known volume. A 25 mℓ portion of the solution was analysed for H_3BO_3 as described above and the corresponding weight of BF_3 was calculated.

Determination of PF_5

The $SF_4.PF_5$ complex was decomposed by adding diethyl ether, SF_4 was set free and $PF_5:Et_2O$ was formed. From this system most of the SF_4 was removed by distillation under vacuum at a low temperature. The residue consisting of $PF_5.(C_2H_5)_2O$ and a little SF_4 was then hydrolysed with an excess of NaOH and made up to 250 mℓ. From the solution PO_4^{3-} was precipitated as ammonium phosphomolybdate 128,129). A 10 mℓ portion of the solution was heated to 60° and 125 mℓ of the ammonium molybdate reagent (Chapter 11), also warmed to 60°, were run into it and maintained at that temperature for one hour with frequent stirring. The precipitate was collected in a weighed porcelain filtering crucible using two 20 mℓ portions of 2 per cent ammonium nitrate solution to transfer it from the beaker, then the precipitate was washed with five 10 mℓ portions of 2 per cent ammonium nitrate solution. The precipitate was dried at 280° and weighed as $(NH_4)_3(PMo_{12}O_{40})$. The amount of PF_5 was calculated from the weight of the ammonium phosphomolybdate.

TABLE 7

Weight in g. of boric acid present in the simulated solution.	Weight in g. of boric acid determined in the simulated solution
0.1624	0.1624
0.1624	0.1628
0.1624	0.1631
0.1624	0.1628

Determination of AsF_5 via AsO_4^{3-}

The $SF_4.AsF_5$ adduct was decomposed with diethyl ether. The liberated SF_4 was separated by distillation under vacuum at about -40°. The residue in the reaction vessel consisting of $AsF_5.(C_2H_5)_2O$ and some dissolved SF_4 was hydrolysed by an excess of aqueous sodium hydroxide. The following procedure was employed to determine AsO_4^{3-} iodometrically$^{129)}$. Since the solution also contained SO_3^{2-} it was probable that AsO_4^{3-} would have been partially reduced to arsenite during the hydrolysis. Therefore, 30% hydrogen peroxide was added to the solution to oxidise SO_3^{2-} and arsenite. The solution was boiled to decompose excess of H_2O_2 and then acidified with hydrochloric acid. A small amount of white gelatinous precipitate was formed which did not dissolve even on boiling. Potassium iodide was then added to the solution and it was allowed to stand for five to ten minutes. Only a very small amount of iodine was liberated - it coloured the solution pale yellow. This observation suggested that either $AsF_5.(C_2H_5)_2O$ was not hydrolysed to Na_3AsO_4 or AsO_4^{3-} formed some sort of complex with ether, which could not be reduced by KI in acidic medium. Therefore, concentrated nitric acid in the presence of sulphuric acid was used as an oxidant, because it could destroy organic matter. But the presence of large amount of F^- was a difficulty because arsenic could be lost as AsF_5. Therefore, the test solution was repeatedly evaporated with concentrated $HC\ell$ to remove all the F^- 132). Then a mixture of concentrated HNO_3 and H_2SO_4 was added and the solution was evaporated slowly to dense white fumes of SO_3. After cooling the solution was diluted and 5N $HC\ell$ was added.

When KI was added to the warm solution a large amount of iodine was liberated as indicated by the dark colour of the solution. Consequently this procedure was adopted for the determination of AsF_5 via AsO_4^{3-} in the test solution. However, to check the reliability of the method a standard solution of sodium arsenite dissolved in excess of NaOH containing SO_3^{2-} , F^- and ether was made and arsenite was determined as AsO_4^{3-} as detailed below.

A 25 mℓ portion of the simulated solution was taken in a glass stoppered conical flask. The solution was evaporated twice with 20 mℓ of concentrated HCℓ until the volume was reduced to 10 mℓ. Finally it was evaporated with 20 mℓ of concentrated HNO_3 and 4 mℓ of concentrated H_2SO_4 to dense white fumes of SO_3. The solution was cooled, diluted with 10 mℓ of water and again evaporated to dense white fumes, in order to ensure the destruction of nitric acid. Finally the solution was diluted with 10 mℓ of water and 5 mℓ of 5 N HCℓ were added. The solution was heated on a water bath to expel air, then about 2 gms of potassium iodide were added and the stopper was quickly replaced. The solution was heated on a steam bath for a further period of 5 to 10 minutes. It was cooled rapidly, diluted to about 50 mℓ and titrated with decinormal sodium thiosulphate solution using a few drops of starch solution as indicator. If the solution is not diluted the thiosulphate decomposes. The results were found to be reproducible and are given in Table 8.

The test solution obtained by hydrolysing $AsF_5.(C_2H_5)_2O$ and SF_4 was treated similarly for the determination of AsO_4^{3-}. From the amount of AsO_4^{3-} the corresponding quantity of AsF_5 was calculated.

TABLE 8

Weight in g. of As_2O_3 present in 10 mℓ of the simulated solution.	Weight in g. of As_2O_3 in 10 mℓ of the simulated solution found.
0.1558	0.1554
0.1558	0.1569
0.1558	0.1561
0.1558	0.1554

Determination of SiF_4 via Silica

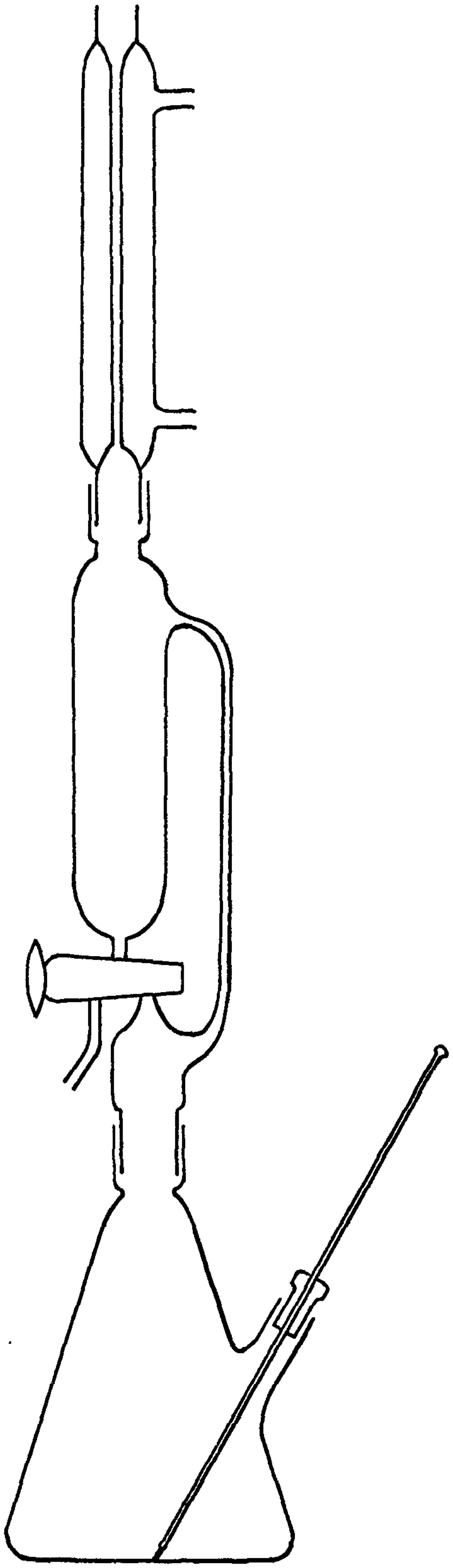
While discussing the determination of SO_4^{2-} in the presence of soluble silicate it was stated that when $SiF_4.(DMF)_2$ is hydrolysed with aqueous NaOH the resulting solution contains F^- and some stable complex of silicic acid with dimethyl formamide. Due to these factors standard methods for the determination of SiO_2 [128,129] did not give satisfactory results. In order to drive out DMF the solution was made strongly alkaline evaporated to dryness and heated at 250°- 280° for two hours. Then the residue was used for the determination of SiO_2 by standard procedure, i.e. evaporating the solution or residue with $HC\ell O_4$ saturated with H_3BO_3, but the results were surprisingly low. Alternatively the solution was evaporated to dryness in a platinium dish, then ignited to oxidise the organic matter. Silica was determined in the residue according to the set procedure[128], but still the results were about 15 per cent lower than the calculated.

Finally wet oxidiation of the organic constituent with mixed HNO_3 and $HC\ell$ and ammonium perchlorate[133] was tried. The reactions involved fall into three categories: (a) Initial conversion of $(NH_4)C\ell O_4$ to $HC\ell O_4$. The reaction with mixed $HC\ell$ and HNO_3 converts the NH_4^+ to N_2O and water. An amount of water approximately equal to the combined mixed acids volume is added to the sampling mixture. The solution is then heated to a temperature of 90° - 100° in not less than five minutes. The reaction is mildly exothermic and is conducted under reflux. It is completed in about ten minutes at a maximum temperature of 110°. All the $HC\ell$ is consumed in this stage. (b) The dilute solution of mixed nitric and perchloric acids gradually concentrates over the temperature range 110° to 150°. The reaction is exothermic and its extent depends upon the nature of organic matter being oxidised. During this step the nitric acid gradually increases in concentration. The oxidation potential of HNO_3 increases gradually to its maximum value at 150° by which time all the organic matter capable of destruction by HNO_3 has been reacted upon and excess HNO_3 has been volatalised. (c) The final stage completes the oxidation of remaining organic matter. At 150° $HClO_4$ first becomes effective. As the temperature rises because of increasing concentration, the oxidation potential increases from approximately 0.8 to 2.0 volts. The perchloric acid concentration increases from 50 per cent at 150° to 72.5 per cent at 203°. The reaction in this stage becomes increasingly exothermic. The complete oxidation of the organic constituent depends upon its nature.

When an organic substance containing small quantities of inorganic constituents is oxidised by ignition a serious loss of the inorganic material usually occurs at high temperature, but in the oxidation by the wet method no such loss takes place. In this procedure the reactions take place under easily adjustable conditions which can be manipulated to longer reaction periods and the full possible effect of nitric acid as an oxygen donor is obtained. The entire procedure requires little attention, no protective screens are required and no explosions have occurred in the use of this method.

However, in the present work this procedure was modified a little, due to the presence of large amount of F^- and the great resistance of dimethyl formamide towards oxidation. In order to check the reliability, accuracy and reproducibility of the modified method a standard solution of Na_2SiO_3 containing SO_3^{2-}, F^- and dimethyl formamide was made and SiO_2 was determined as detailed below.

A 25 mℓ portion of the simulated solution was taken in the flask (Bethge Apparatus) (Fig.9). The solution was made strongly alkaline, evaporated to dryness and then heated at 250° for one hour in order to expel as much organic matter as possible. Then to the residue were added 7.5 mℓ of concentrated HCℓ, 18 mℓ of concentrated HNO_3, 16 gms of $NH_4CℓO_4$, 20 mℓ of water and 1 g. of H_3BO_3. The reaction mixture was heated under reflux until the temperature reached 110° in about ten minutes. The heating under reflux was continued for two to three hours in order to hydrolyse dimethyl formamide. Then the condenser was removed and heating continued, but arrangement was made to let the condensate return to the flask. The water vapours and other volatile constituents slowly escaped into the atmosphere and the perchloric acid gradually concentrated over the temperature range 110° to 150°. This step took about three hours. The contents were kept at 150° for about fifteen minutes and the heating rate was increased till the temperature climbed to 205°. The mixture was heated at this temperature for two hours in order to ensure the complete oxidation of the organic constituents. After cooling, the contents of the flask were carefully washed out into a 600 mℓ beaker. The beaker was heated over a steam bath for several hours to settle the finely divided silica. The clear solution was decanted through a Whatman filter paper No.40; maximum care was taken to let minimum amount of the precipitate go to the filter paper. About 1 mℓ of concentrated H_2SO_4 was added to the residue and it was evaporated to dense white fumes in order to dissolve adsorbed H_3BO_3. After cooling, it was



BETHGE APPARATUS

FIG: 9

diluted with 50 mℓ of water, heated on a steam bath and the clear solution was decanted through the original filter paper. The filter paper was ignited in a weighed platinium cruicible. The exact SiO_2 content was determined by volatalising SiO_2 with HF and then weighing the platinium cruicible$^{128,129)}$. The results are given in Table 9.

The test solution containing dimethyl formamide and hydrolytic products of SiF_4 and SF_4 was analysed by the above procedure. The amount of SiF_4 was calculated from the weight of SiO_2 determined for SiO_2. The results were in agreement with the calculated values.

Determination of SeF_4 via H_2SeO_3

A known volume of the sodium selenite solution obtained by hydrolysing SeF_4 was oxidised with excess $KMnO_4$ in acidic medium and the excess $KMnO_4$ was determined by titrating with ferrous ammonium sulphate$^{129)}$.

<u>TABLE 9</u>

Weight in g. of $Na_2SiO_3.9\ H_2O$ in 500 mℓ of the solution	Calculated weight in g. of SiO_2 in 25 mℓ of the solution	Weight in g. of SiO_2 in 25 mℓ of the solution found
14.5300	0.1536	0.1540
	0.1536	0.1528
	0.1536	0.1522

CHAPTER 5

Investigation of the Complex $SF_4.BF_3$

Introduction

Bartlett and Robinson[23,24)] suggested that the complex $SF_4.BF_3$ was simple Lewis acid-Lewis base type because SF_4 has a lone pair of electrons that would form a coordinate bond with BF_3, and was unlikely to be an ionic compound because there was no evidence for the formation of a stable SF_3^+ ion from SF_4. However, they suggested that the analogous SeF_4 compound might be ionic, e.g. $SeF_3^+ BF_4^-$ [23,24)], because there is evidence for the SeF_3^+ ion in that, the electrical conductivity of SeF_4 indicates it is self-ionized to SeF_3^+ and SeF_5^- [23,24)]. The Lewis acid-Lewis base formulation of $SF_4.BF_3$ was criticised by Cotton and George[18)] on theoretical grounds. They proposed that SF_4 would be expected to be a poorer donor than PF_3 for two reasons. Firstly, in PF_3 there are only three fluorine atoms tending to decrease the donor strength of the lone pair whereas in SF_4 there are four. Secondly, there should be more steric hindrance in SF_4 than in PF_3. Nevertheless, although the SF_4 adduct is stable at room temperature Booth and Walkup[8,18,36)] have shown by thermal analysis that even in the range -140° to -165° PF_3 does not form an adduct with BF_3. These authors therefore, suggested that the adduct $SF_4.BF_3$ would not be expected to be a donor acceptor type complex. They advanced the following additional argument to strengthen their hypothesis "while BF_3 can function as a fluoride acceptor giving BF_4^- and as a general Lewis-acid, and AsF_5 and SbF_5 are known to be very strong F^- acceptors, i.e. acids in the HF system, there is little evidence to show that the latter are also good general Lewis-acids. Consequently, it seems reasonable to postulate that the AsF_5 and SbF_5 adducts of SF_4 are actually SF_3^+ AsF_6^- and SF_3^+ SbF_6^- and, therefore, these compounds imply the ability of SF_4 to form ionic adducts containing SF_3^+ ions. Moreover, it has recently been shown that the strongest acids in HF, i.e. the best F^- acceptors are AsF_5, SbF_5 and BF_3 127)." However, the foregoing argument is not sound because AsF_5 and SbF_5 do in fact form (1:1) addition compounds46) with many organic substances containing a donor atom, i.e. S, N or O, showing that AsF_5 and SbF_5 are indeed general Lewis acids.

Cotton and George also stated that "the absence of appreciable self-ionization according to

$$2SF_4 \rightleftharpoons SF_3^+ + SF_5^-$$

could be due entirely to the inability of SF_4 to add a fluoride ion to form SF_5^- and thus not indicate any marked inability to form SF_3^+ ". However, this argument is also invalid, because it has been shown recently that SF_5^- 22) is stable at room temperature.

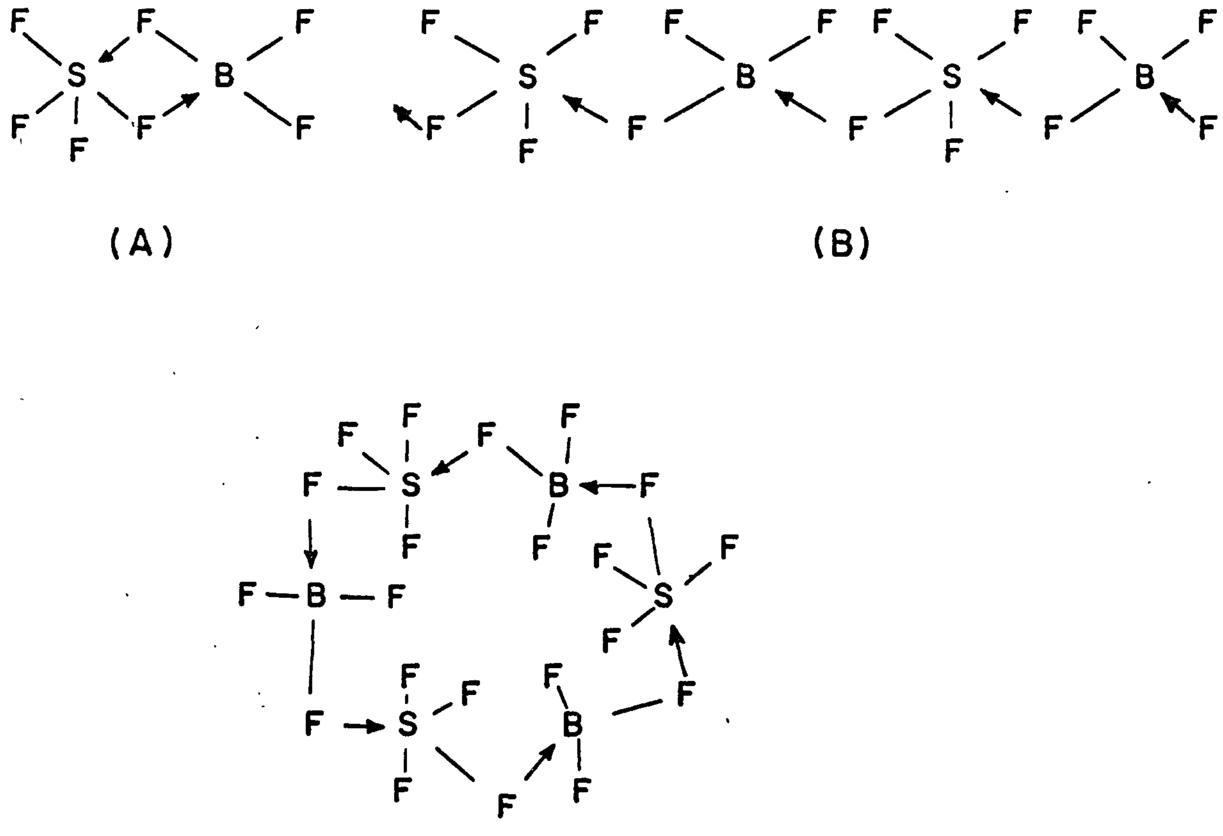
It was pointed out by Stone18) that if both the SF_4 and SeF_4 adducts with BF_3 were donor acceptor complexes, the observed order of stability (Se>S) would be contrary to the general rule that Lewis basicity decreases in descending a group of analogous donors. However, it should be added that this stability order argument would be irrelevent if the SF_4 adduct were a donor acceptor complex while the SeF_4 adduct were ionic. Cotton and George18) examined the I.R.

spectrum of the complex, but the results proved to be inconclusive due to the instability and reactivity of $SF_4.BF_3$. They prepared nujol mulls and KBr pellets of the adduct for spectroscopic examination, but even using dry box techniques, decomposition and/or reaction of the material was always encountered. This difficulty could be related to the moderate vapour pressure of $SF_4.BF_3$ at room temperature, and the extreme sensitivity of SF_4 to traces of moisture. Consequently the spectra obtained were not necessarily representative of the $SF_4.BF_3$ species. While an indication of the BF_4^- ion was obtained it could not be taken as structural proof since hydrolysis involving $SF_4.BF_3$ would certainly give rise to the BF_4^- ion. These authors also prepared a sample of $SF_4.BF_3$ by condensing the adduct on a silver chloride plate maintained in a vacuum cell at liquid nitrogen temperature. The spectra obtained were either blank or were the spectra of the components SF_4 and BF_3 or the impurities SOF_2 and SiF_4. The difficulty in obtaining a spectrum representative of $SF_4.BF_3$ was ascribed to large particle size of the solid $SF_4.BF_3$, which condensed on the $AgC\ell$ plate, while volatalization of the sample and reaction with moisture and/or pyrex lead to the presence of gaseous species.

Seel and Detmer27) were, however, able to obtain the infrared spectrum of the adduct, although they do not give experimental details such as sample preparation and the type of l.R. cell employed. They found an absorption band at 1051 cm^{-1} which is typical of BF_4^- and of greater significance, because BF_4^- can arise by the reactions of the fluorides with $NaC\ell$ windows1) used in this investigation, a doublet at 908 and 940 cm^{-1} which by comparison with PF_3 was assigned to the SF_3^+ ion. The technique used for preparing solid $SF_4.BF_3$ sample for taking the I.R. spectrum is very significant because the compound is extremely reactive towards mositure and its vapour pressure at room temperature is 112 mm[27)]. Due to the dissociation and high vapour pressure of the solid it is almost impossible to record the I.R. spectrum of a solid sample of $SF_4.BF_3$ at room temperature.

Lack of evidence for the ionization of SF_4 by fluorine anion transfer, the low thermal stability of $SF_4.BF_3$, its insolubility in non-polar and polar solvents except HF[134)], and the above discussed experimental and theoretical evidence suggest that the ionic formulation of $SF_4.BF_3$ is questionable. In addition to the donor-acceptor and ionic formulations it is possible to envisage another covalent structure in which there are fluorine bridges. The structure of $SF_4.BF_3$ may be intermediate between the ionic and the covalent formulation. Possible alternative structures for $SF_4.BF_3$ involving bridging fluorine atoms are given in Fig.10. An infinite polymeric structure such as that represented by B (Fig.10) would account for the general insolubility of the compound. If the ionic structure were correct the compound would be expected to dissolve in anhydrous ionizing solvents.

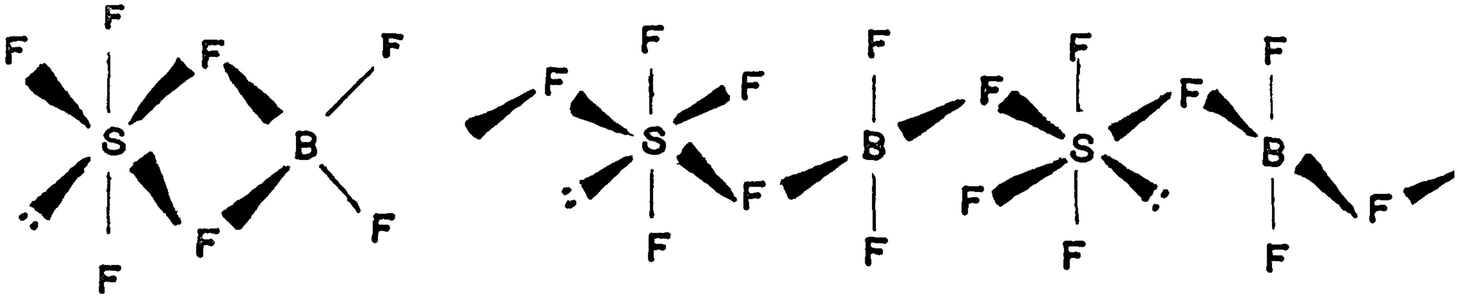
The geometric shapes of the $SF_4.BF_3$ molecule (Fig.10A) or polymeric units (10B and 10C) based on the above covalent structures would be expected to be as shown in Figs. 11A and 11B respectively. In the structure shown in Fig.10A the sulphur atom acquires six electron pairs in the valency shell, of these one pair of electrons is unshared, therefore, the shape of this part of the molecule would be based on an irregular octahedron[135)]. The boron atom has four electron pairs,



(A) (B)

(C)

FIG·10



(A) (B)

FIG·11

all shared, in its valency shell, therefore, it would have a tetrahedral arrangement of fluorine atoms around it[135]. In other words the octahedral sulphur atom would share an edge with the tetrahedral boron atom (Fig.11A). In the alternative polymeric structure (10B and 10C) the boron and sulphur atoms would have tetrahedrally and octahedrally co-ordinated fluorine atoms including a lone pair of electrons, and the $SF_4 \cdot BF_3$ polymer would be either in the form of a chain (Fig.10B) or a ring (Fig.10C) having alternate octahedra and tetrahedra sharing a corner (Fig.11B). However, in the former case the boron atom at one end of the chain would be expected to be tetrahedral and the sulphur atom at the other end of the chain would have a trigonal bipyramid arrangement of four bonds and a lone pair of electrons.

In the present work the structure of this complex has been reinvestigated employing F^{18} as a tracer, infra-red spectroscopy and fluorine nuclear magnetic resonance spectroscopy.

F^{18}- Exchange Studies

By preparing the complex with one of the components labelled with F^{18}, then decomposing the compound by tetrahydrofuran or other nucleophiles and determining the radioactivity in the products of decomposition (BF_3 and SF_4), it is in principle possible to differentiate between Lewis acid-base, the ionic and the covalent structures for the complex. If the complex involves a simple co-ordinate bond between the sulphur and the boron atoms there should be no exchange of F^{18} between the two components. However, exchange of fluorine between the two components would be expected for either the ionic structure or the fluorine-bridged structures. As explained later it is in principle also possible to differentiate between these two structures.

The tracer investigation of the structure of $SF_4.BF_3$ was carried out in two parts. In the first set of experiments BF_3^{18} was used for making $SF_4.BF_3$ and in the second set SF_4^{18} was employed. The experiments were done at several temperatures between room temperature and -100°.

Exchange of Fluorine-18 between SF_4 and BF_3^{18}. Tetrahydrofuran Co-ordination Complex

Before commencing the study of the fluorine-18 exchange reactions between BF_3 and SF_4 in the adduct it was considered necessary to investigate the possible exchange of radioactive fluorine between SF_4 and BF_3^{18}.THF.

The BF_3^{18}, prepared according to the method described in Chapter 3, was first condensed in the trap T (Fig.8) and then evaporated at -100° into the bulb C(Fig.8) until it was filled with the gas at atmospheric pressure. Then the BF_3^{18}, about 550 $m\ell$ at atmospheric pressure, was condensed into the reaction vessel D (Fig.7), cooled in liquid air, followed by addition of 4 $m\ell$ of tetrahydrofuran by means of the 'cold funnel' (Fig. 34). On warming the contents of D to room temperature a clear solution was obtained. The solution was cooled to about -80° in a dry ice acetone bath and pumped to remove any unreacted BF_3^{18}. The reaction vessel D was again cooled to liquid air temperature and about 500 $m\ell$ of SF_4 at atmospheric pressure were condensed into it. The stop cock 1 (Fig.7) was closed and the reaction vessel was warmed successively to -80°, -40° and -5°, and kept at each temperature for fifteen minutes, during which time SF_4 was collected in a receiver 'E'. At every temperature SF_4 was collected into a fresh receiver 'E'. The residue in the reaction vessel D (IV) and the three fractions of SF_4, I (-80°), II (-40°) and III (-5°), were hydrolysed by an excess of ice-cold NaOH solution (16 per cent) and each solution was diluted with water to 250 mℓ. A 5 mℓ aliquot from each of these solutions was counted for fluorine-18 as described in Chapter 2.

Each solution of SF_4 was tested for boron with turmeric[132)].* The solution I gave a very faint pink colour, but the other two showed strong colour reaction and the solution IV obtained from BF_3:THF gave a negative test for SO_4^- i.e. SF_4 was absent. Therefore, the SF_4 solutions were analysed for boron according to the procedure described in Chapter 4 and the amount of BF_3^{18} in each solution was calculated. The results of this experiment are given in Table 10. The amounts of BF_3 found in these solutions accounted for the F^{18} activity, as can be seen in columns II and IV (Table10). It was, therefore, concluded that there is no F^{18} exchange between SF_4 and BF_3^{18}. THF at -80°, -40° or -5°.

Determination of specific activity of BF_3^{18}

In order to check the accuracy of the results of the exchange reactions the specific activity of BF_3^{18} was determined in each set of

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* By this method 0.02μg. of boron can be detected in a concentration 1:2, 500, 000.

TABLE 10

Exchange of F^{18} between $BF_3^{18}.THF$ and SF_4

Solution	I Counts per minute in 5 mℓ of the solution	II Counts per minute in 250 mℓ of the solution	III Counts per minute in 250 mℓ of the solution calculated from the amount of BF_3	IV Weight in g. of BF_3 found.
SF_4I (-80°)	49.3	2,465	2,929	0.0017
SF_4II (-40°)	440	22,000	20,997	0.1221
SF_4III (-5°)	520	26,000	24,400	0.1424
BF_3 (THF) Residue	3,600	180,000	188,000	1.092
BF_3.THF + SF_4 (I,II,III)	4,609	230,000	234,000	1.3582
Counts $min.^{-1}$ $g.^{-1}$ for BF_3		172100		

experiment as follows. The bulb C (Fig.8) was filled with BF_3^{18} at atmospheric pressure and the gas was condensed into the reaction vessel D, cooled in liquid air. The hydrolysis of BF_3 proceeds smoothly if the addition compound with THF is made first. Therefore, about 5 mℓ of THF was added to the BF_3^{18} condensed in D and then warmed to 0°. The adduct BF_3^{18}. THF was then hydrolysed with an excess of ice-cold sodium hydroxide solution (16 per cent). The solution was made up to 250 mℓ and 5 mℓ of the solution was counted for F^{18}. Boron trifluoride was determined via H_3BO_3 (Chapter 4) and the specific activity was calculated at some convenient time.

It will be noted that the solutions containing BF_3 were hydrolysed by aqueous alkali while hydrolysis by water would have been preferable because the estimation of boron in acid solution is simple and more rapid. Alkaline hydrolysis was necessary for the following reason. The solutions were radioactive and could not be analysed immediately. If free HF were present in the solution it would attack the glass giving silicic acid which would result in high values in the boron determination.

Exchange of F^{18} between BF_3^{18} and SF_4 in gas phase

An attempt was made to investigate F^{18} exchange between BF_3^{18} and SF_4 in the gas phase. The bulb C (Fig.8) was filled with BF_3^{18} and then SF_4 was introduced into it. As soon as the two gases came in contact solid $SF_4.BF_3$ was deposited on the walls of the bulb C and the level of mercury column rose, showing that $SF_4.BF_3$ is formed on mixing the two gases at room temperature. Further investigation of this exchange was considered unnecessary because the results were expected to be the same as in the following experiments.

Exchange of F^{18} between SF_4 and BF_3^{18} on the formation of the solid adduct

Equal volumes of purified SF_4 and BF_3^{18} were condensed in the reaction vessel D (Fig.7) cooled in liquid air. The reaction vessel was slowly warmed to room temperature. The complex was formed as soon as the SF_4 melted and the reaction between liquid SF_4 and liquid BF_3 was observed to be exothermic. The complex was then pumped for a few minutes to remove any unreacted components and maintained at room temperature for thirty minutes and then again cooled in liquid air. After adding about 10 mℓ of anhydrous tetrahydrofuran the reaction vessel was warmed to -20° and the SF_4 set free was collected for about five minutes in the receiver E (Fig.7) cooled in liquid air. The contents of the reaction vessel D and the receiver E were hydrolysed with an excess of ice-cold NaOH solution (16 per cent) and made up to a known volume, usually 250 mℓ. For the determination of specific activity of BF_3^{18}, the solution of the gas was made as described earlier. A 5mℓ portion of each solution was then counted for F^{18} and the activity of each solution was determined at a convenient time. The solutions were analysed according to the methods described in Chapter 4 and from the analytical and counting data the percentage of F^{18} activity of the boron trifluoride transferred to the SF_4 was calculated. The results* are given in Table 11.

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* The accuracy of the counting data is ± 3 per cent.

TABLE 11

F^{18} Exchange in 30 minutes between SF_4 and BF_3^{18} in $SF_4.BF_3^{18}$ at room temperature

		I	II	III
1.	Counts $min.^{-1}$ $g.^{-1}$ for BF_3^{18} at zero time.	80533	27610	1244900
2.	Weight in g. of BF_3^{18} in $SF_4.BF_3^{18}$.	1.4412	1.4179	1.4373
3.	Weight in g. of SF_4. in SF_4 BF_3^{18}.	2.2840	2.2547	2.2888
4.	Weight in g. of SF_4 separated from $SF_4.BF_3$ using THF at zero time.	1.2489	0.7518	0.8638
5.	Counts $min.^{-1}$ for the SF_4 separated at zero time.	35537	6845	391775
6.	Counts $min.^{-1}$ for the residue at zero time.	80875	30500	1425000
7.	Counts $min.^{-1}$ for BF_3^{18} in $SF_4.BF_3^{18}$ at zero time. (sum of 5 and 6).	116412	37345	1816775
8.	Counts min^{-1} for BF_3^{18} in $SF_4.BF_3^{18}$ at zero time. (1 and 2).	116062	39148	1789250
9.	Total counts $min.^{-1}$ transferred to (3,4 and 5) the SF_4.	64989	20528	1038078
10.	Percentage of F^{18} transferred to SF_4 (7 and 9).	55.8	55.0	57.1

The hydrolysed solution of SF_4 collected in E gave a negative reaction when tested for boron132), thus showing that the radioactivity in SF_4 was not due to contamination with BF_3^{18}. On the other hand in the discussion regarding the transfer of F^{18} between BF_3^{18}. THF and SF_4 it was stated that even at low temperatures traces of BF_3 distilled over with SF_4 because BF_3.THF had a small vapour pressure. Apparently these two statements contradict each other. However, it should be pointed out that in the former case (F^{18} exchange between SF_4 and BF_3^{18}. THF) the amount of tetrahydrofuran used was only slightly in excess of the required stoichiometric quantity while in the latter a large excess of THF was added which dissolved the BF_3·THF complex as well as the SF_4. On distilling the mixture under vacuum at low temperature (-20° to -30°) it would be expected that the solvent along with SF_4 (b.p. -40.4°) would voltalize first and BF_3.THF would distil only when all the solvent has been removed.

The exchange reaction was also carried out at lower temperatures, viz: -15°, -30°, -40°, -60°, -80° and -100°. In these experiments the same apparatus and procedure were used as described earlier. After forming the complex as described above it was allowed to stand at a given temperature for the desired length of time, i.e. 5, 10, 20 or 60 minutes, and then it was chilled quickly in liquid air. About 4 mℓ of anhydrous tetrahydrofuran contained in the 'cold' funnel was cooled by dry ice and slowly added to the adduct. Then the reaction vessel was put in an n-pentane bath (-130° to -110°) and slowly warmed to the temperature at which the adduct SF_4·BF_3^{18} had been allowed to stand. About 10-15 minutes were allowed to complete the reaction between $SF_4.BF_3^{18}$ and tetrahydrofuran. The SF_4 displaced by THF was collected in the receiver E for 10-15 minutes. After the reaction was over the contents of D and E were hydrolysed with excess of ice-cold NaOH solution (16 per cent) and the solutions were made up to a known volume. In every experiment a solution of BF_3^{18} was prepared for the determination of specific activity. The solutions were counted and analysed according to the methods described in the preceding chapters and the percentage of the F^{18} transferred to SF_4 was calculated. The SF_4 collected in E contained a small amount of boron whose precurser was BF_3^{18}. Correction for the extraneous activity due to BF_3^{18} was made as follows. The amount of BF_3 present in the SF_4 solution was determined. The activity of the BF_3 found was calculated from the specific activity data; let it be X cpm. The activity of BF_3^{18}, X cpm, was then subtracted from the activity of SF_4 (collected in E), and the percentage of F^{18} activity transferred to the SF_4 was calculated; let it be A. It should be taken into consideration that BF_3^{18} which was carried over by SF_4 (collected in E) had exchanged some of its activity with SF_4. Therefore, in the next step $(X - \frac{AX}{100})$ cpm. were subtracted from the activity of the SF_4 obtained by counting. The corrected activity of the SF_4 was then used for determining the exchange percentage of fluorine 18. A second order correction can be applied if necessary.

The exchange of F^{18} between the two constituents in $SF_4.BF_3^{18}$ was repeated at -80° using anhydrous diethyl ether for displacing SF_4 from the adduct. The experimental arrangement and conditions were the same as used in the corresponding experiments with tetrahydrofuran.

The results of these experiments are given in Tables 12, 13 and 14 .

A plot of fluorine-18 exchange vs. temperature is shown in Fig.12. The amount of the exchange decreased from approximately 56 per cent at room remperature, to approximately 16 per cent at -80°. The percentage of F^{18} exchange in an experiment carried out at -100° was also found to be of the same order as the exchange at -80°. The amount of exchange of F^{18} at -80° was independent of the time of the exchange reaction over the periods 5 to 60 minutes (Tables 13 and 14).

Exchange of F^{18} between $SF_4{}^{18}$ and BF_3 on the formation of the solid adduct $SF_4{}^{18}.BF_3$

To check the conclusions drawn from the results of the preceding experiments the exchange was studied using $SF_4{}^{18}$. The experiments were done at room temperature, -60° and -80°. The experimental arrangement and conditions were the same as in the corresponding experiments using $BF_3{}^{18}$. In this set of experiments anhydrous ether was used for decomposing the adduct $SF_4{}^{18}.BF_3$. Sulphur tetrafluoride was labelled with fluorine-18 by solid-gas phase exchange reaction between LiF^{18} and SF_4 (Chapter 3). The specific activity of $SF_4{}^{18}$ was determined by a method analogous to that of $BF_3{}^{18}$. The results of this exchange study are given in Table 15.

TABLE 12

F^{18} Exchange between SF_4 and BF_3^{18} in $SF_4 \cdot BF_3^{18}$ - Temperature Dependence

$SF_4 \cdot BF_3^{18}$ decomposed by tetrahydrofuran. Exchange reaction time 20-30 minutes

		-15°	-30°		-40°		-60°
			I	II	I	II	
1.	Counts min.$^{-1}$ g.$^{-1}$ for BF_3^{18} at zero time.	454232	952940	2850000	23698	6462	31205
2.	Weight in g. of BF_3^{18} in SF_4 BF_3^{18}.	1.276	1.5216	0.9425	1.5266	1.5052	1.1055
3.	Weight in g. of SF_4 in $SF_4 \cdot BF_3^{18}$.	2.0319	2.423	1.5085	2.4788	2.3969	1.7604
4.	Weight in g. of SF_4 separated from $SF_4 \cdot BF_3^{18}$ using THF.	1.0656	.0307	.0097	2.1164	.4935	0.7823
5.	Counts min.$^{-1}$ for the SF_4 separated at zero time.	147720	7725	7850	10036	724	4145
6.	Counts min.$^{-1}$ for the residue at zero time.	431500	1370000	2692500	25454	8886	29900
7.	Counts min.$^{-1}$ for BF_3^{18} in $SF_4 \cdot BF_3^{18}$. (sum of 5 and 6).	5799220	1377725	2709350	35490	9610	34045
8.	Counts min.$^{-1}$ for BF_3^{18} in $SF_4 \cdot BF_3^{18}$ at zero time (1 and 2).	579600	1450000	2684700	36177	9726	34497
9.	Counts min.$^{-1}$ transferred to the SF_4 (3,4 and 5)	281674	608907	1220796	11754	3516	9327
10.	Percentage of F^{18} transferred to SF_4 (7 and 9).	48.6	44.2	45.1	33.1	36.6	27.4

TABLE 13

F^{18} Exchange between SF_4 and BF_3^{18} in $SF_4.BF_3^{18}$ at -80°. $SF_4.BF_3^{18}$ decomposed by tetrahydrofuran. Time of exchange reaction 20 minutes.

		I	II	III	IV
1.	Counts cm.$^{-1}$ g.$^{-1}$ of BF_3^{18} at zero time.	356376	615058	123460	346090
2.	Weight in g. of BF_3^{18} in $SF_4.BF_3^{18}$.	1.5570	1.2950	1.4344	1.4853
3.	Weight in g. of SF_4 in $SF_4.BF_3^{18}$.	2.4787	2.053	2.2853	2.3753
4.	Weight in g. of SF_4 separated from $SF_4.BF_3^{18}$ using THF.	0.0390	0.7471	0.5499	0.2696
5.	Counts min.$^{-1}$ for the SF_4 separated at zero time.	1210	50400	72700	9490
6.	Counts min.$^{-1}$ for the residue at zero time.	530000	706950	1618800	485860
7.	Counts min.$^{-1}$ for BF_3^{18} in $SF_4.BF_3^{18}$ at zero time . (sum of 5 and 6).	531210	757350	1691500	495350
8.	Counts min.$^{-1}$ for BF_3^{18} in $SF_4.BF_3^{18}$ at zero time (1 and 2).	554720	796500	1771000	51447
9.	Total counts min.$^{-1}$ transferred to the SF_4 (3, 4 and 5).	76903	137947	302130	83611
10.	Percentage of F^{18} transferred to SF_4 (7 and 9)	14.5	18.2	17.9	16.8

TABLE 14

F^{18} Exchange between SF_4 and BF_3^{18} in $SF_4.BF_3^{18}$ at -80° and -100°. Time Dependence.

$SF_4.BF_3^{18}$ decomposed by ether

		10 minutes	30 minutes	5 minutes	60 minutes	10 minutes at -100°
1.	Counts $g.^{-1}$ $min.^{-1}$ for BF_3^{18} at zero time.	91575	198725	141645	200250	103000
2.	Weight in g. of BF_3^{18} in $SF_4.BF_3^{18}$.	1.2004	1.2309	1.4287	1.3779	1.4975
3.	Weight in g. of SF_4 in $SF_4.BF_3^{18}$.	1.8944	1.9590	2.2779	2.2098	2.3797
4.	Weight in g. of SF_4 separated from $SF_4.BF_3^{18}$ using THF.	0.6652	0.3356	0.4173	0.2976	1.6067
5.	Counts $min.^{-1}$ for the SF_4 separated at zero time.	5700	7615	6195	6565	19825
6.	Counts $min.^{-1}$ for the residue at zero time.	99250	230615	187335	273585	137550
7.	Counts $min.^{-1}$ for BF_3^{18} in $SF_4.BF_3^{18}$ at zero time from counting data (sum of 5 and 6).	104950	238230	193530	280150	157375
8.	Counts $min.^{-1}$ of BF_3^{18} in $SF_4.BF_3^{18}$ at zero time (1 and 2).	109930	244610	202370	275925	154242
9.	Total counts $min.^{-1}$ transferred to the SF_4.	16245	44450	33816	48747	29363
10.	Percentage of F^{18} transferred to SF_4 (7 and 9).	15.5	18.7	17.5	17.4	18.7

TABLE 15

F^{18} Exchange between SF_4^{18} and BF_3 in $SF_4^{18}.BF_3$. Temperature Dependance. $SF_4.BF_3$

Decomposed by THF at room temperature. Time of exchange thirty minutes.

	Room Temperature		-40°	-80°	
	I	II		I	II
1. Counts g.$^{-1}$ for SF_4^{18} at zero time.	43998	35145	89997	18560	---
2. Weight in g. of SF_4^{18} in $SF_4^{18}.BF_3$.	1.6188	1.8213	1.7067	2.2395	2.2098
3. Weight in g. of BF_3 in $SF_4^{18}.BF_3$.	1.0215	1.1517	1.0812	1.4124	1.3927
4. Weight in g. of SF_4 separated from $SF_4^{18}.BF_3$.	1.6531	0.9763	1.3505	1.2192	1.3191
5. Counts min.$^{-1}$ for the SF_4 separated	39800	19000	103720	22280	89280
6. Counts min.$^{-1}$ for the residue at zero time.	30425	43250	51035	22506	77815
7. Counts min.$^{-1}$ for SF_4^{18} in $SF_4^{18}.BF_3$ at zero time (sum of 5 and 6).	69225	62250	154755	44786	167095
8. Counts min.$^{-1}$ for the SF_4^{18} in $SF_4^{18}.BF_3$ at zero time (1 and 2).	71225	64000	153598	41564	---
9. Total counts min.$^{-1}$ transferred to the BF_3 (2, 4, 5 and 7)	30251	26850	53684	3860	18530
10. Percentage of F^{18} transferred to BF_3. (7 and 9).	43.7	43.1	34.7	8.6	11.1

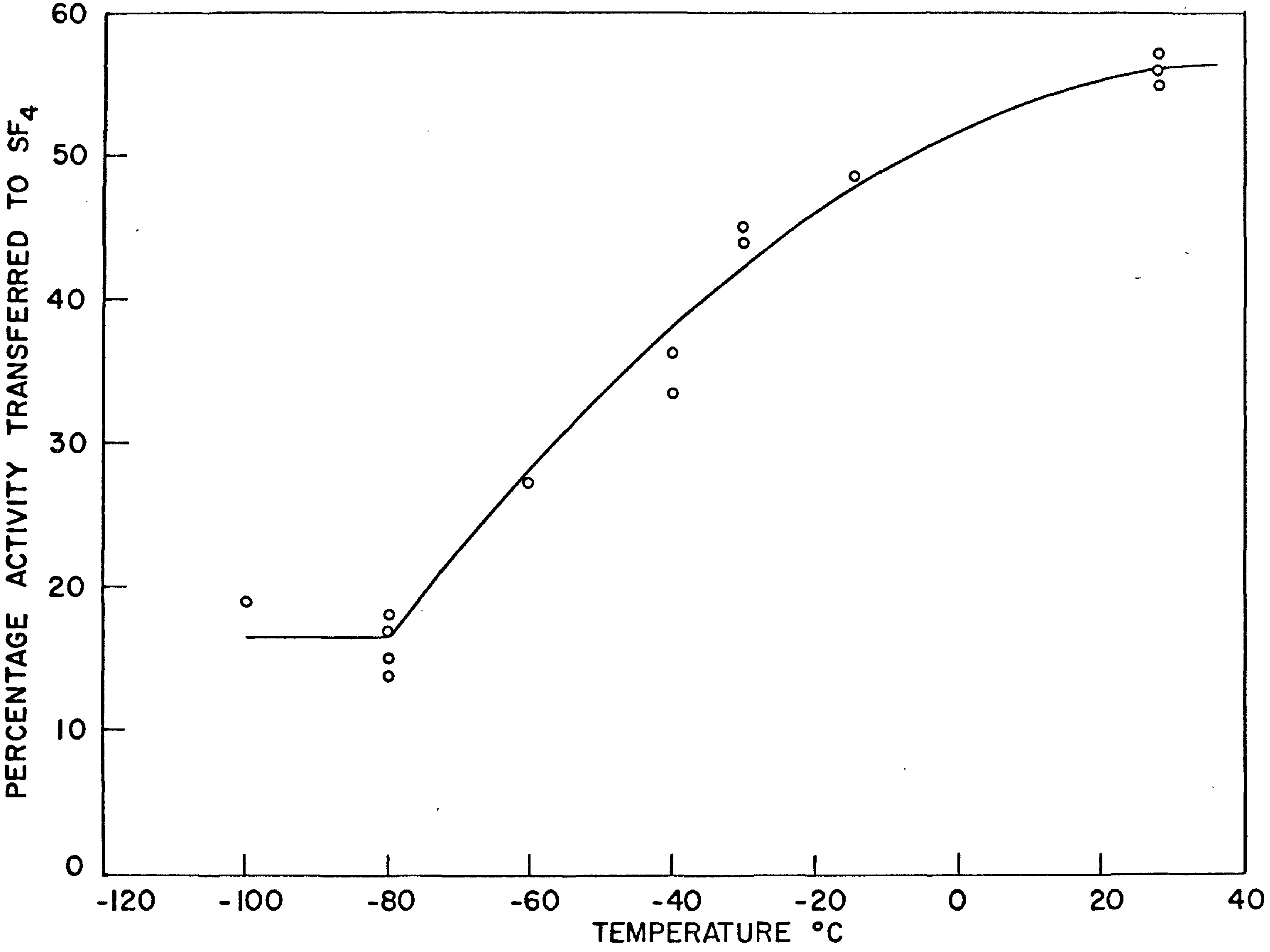

60
50
40
30
20
10
0
PERCENTAGE ACTIVITY TRANSFERRED TO SF_4
-120
-100
-80
-60
-40
-20
0
20
40
TEMPERATURE °C

FIG: 12

Discussion

When BF_3^{18} was used for preparing the adduct $SF_4.BF_3^{18}$ it was found that the F^{18} activity transferred to SF_4 at room temperature and -80° was 55 - 57 per cent (Table 11) and 14.5 - 18 per cent (Tables 13 and 14) respectively and the amount of exchange at intermediate temperatures was between these limits (Table 12). On the other hand, under similar conditions when SF_4^{18} was used for making the adduct the F^{18} activity transferred to BF_3 was 43 - 44 per cent at room temperature, 34 per cent at -40° and 8.6 - 11 per cent at -80° (Table 15).

In the adduct $SF_4.BF_3$ if the fluorine atoms exchange completely between the two components the activity transferred to the non radioactive component would be 57.1 per cent. in the case of $SF_4.BF_3^{18}$ and 42.9 per cent. in the case of $SF_4^{18}.BF_3$. The results of the exchange reactions carried out at room temperature are comparable with the theoretical values. Therefore, it is inferred that at ambient temperature all the fluorine atoms exchange completely between the components of $SF_4.BF_3$. These results allow one to reject the Lewis acid-Lewis base type structure of the adduct which could not lead to any exchange. If exchange occurs on the decomposition of the solid adduct (which as explained below may be either ionic or covalent) and if at room temperature the solid is in rapid equilibrium with the components inthe gas phase, the observed fast exchange can be accounted for by one of the following dissociative mechanisms.

(Ionic Structure) $$\underset{(S)}{SF_3^+} + \underset{(S)}{BF_4^-} \rightleftharpoons \underset{(G)}{SF_4} + \underset{(G)}{BF_3} \qquad (1)$$

(Bridge Structure) $$\underset{(S)}{SF_4.BF_3} \rightleftharpoons \underset{(G)}{SF_4} + \underset{(G)}{BF_3} \qquad (2)$$

Note: S = solid

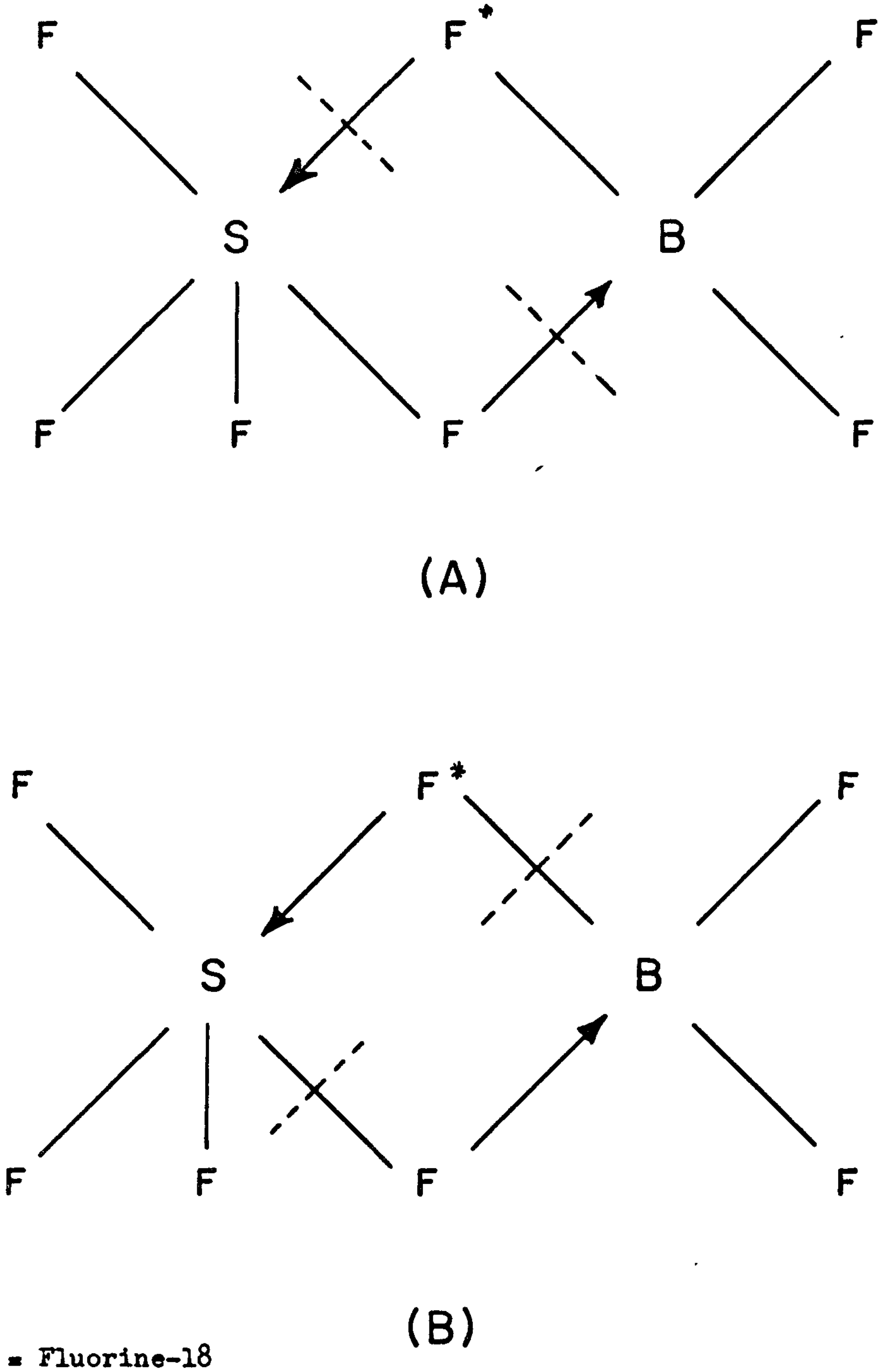
G = gas

In BF_3^{18} one fluorine atom out of three would be expected to be F^{18}. If it is assumed that $SF_4.BF_3^{18}$ is ionic, i.e. SF_3^+ BF_4^-, the BF_4^- ion would have one atom of F^{18} out of four. If it is also assumed that the vapour pressure of the solid is low enough then no appreciable exchange of F^{18} can occur by the above mechanism (1) then on decomposing the complex $SF_4.BF_3^{18}$ with an anhydrous nucleophile, viz: ethers and tertiary amimes, etc. it would be expected that 25 per cent of the F^{18} activity would be transferred to SF_4 provided there is no exchange by other mechanisms.

If the ionic structure is the true formulation of the adduct, $SF_4.BF_3$ the exchange of F^{18} between the two components is possible through the equilibrium (1). In the solid the two ions SF_3^+ and BF_4^- would be held together by electrostatic force and there does not seem to be any mechanism other than the above by which fluorine could migrate from BF_4^- to SF_3^+ and vice versa. The exchange of F^{18} will depend upon the equilibrium constant of the above reversible reaction, which is temperature dependent. Although the vapour pressure of $SF_4.BF_3$ is very small at -50°, i.e. less than 0.1 mm. (Fig.2) it is not until -60° that amount of F^{18} exchange was found to be close to the theoretical value for the ionic model. However, at still lower temperatures amount of exchange decreased further (Tables 13 and 14) indicating that $SF_4.BF_3$ could not be formulated as $SF_3^+ BF_4^-$.

If it is assumed that $SF_4.BF_3^{18}$ has one of the structures involving bridging fluorine atoms, the probability of forming a F^{18} bridge is 33.3 per cent because in radioactive BF_3 one fluorine atom out of three is expected to be radioactive. Presuming that at a low temperature the exchange of F^{18} does not take place via the dissociative mechanism (2) then on decomposing the adduct with a nucleophile the amount of F^{18} exchange would depend upon the relative strengths of the fluorine bridge bonds. If the B-F^{18} bond is broken 33 per cent of F^{18} would be transferred to SF_4, on the other hand if the S-F^{18} bond is broken the SF_4 would be inactive (Fig.13). However, if the two bonds are of comparable strength the probability of breaking either of them might be approximately equal, therefore, on decomposing the adduct by a metathetical reaction 16.7 per cent of the F^{18} activity would be transferred to the SF_4 and the exchange would be expected to be independent of time.

The results of the exchange experiments on $SF_4.BF_3^{18}$ show that as the temperature is lowered the percentage of F^{18} exchange between SF_4 and BF_3^{18} decreased and reached a low value at -80° which fluctuated between 15-19 per cent and is not dependent upon time. Very similar results were also obtained at -100°. These results suggest that the exchange of F^{18} between the two constituents does not take place through the dissociative mechanism and that the exchange occurs on the formation of a fluorine bridged complex $SF_4.BF_3$ (Fig.10).



F* = Fluorine-18

FIG: 13

In labelled SF_4 one fluorine atom out of the four is expected to be F^{18}. If the ionic structure of $SF_4^{18}.BF_3$ is assumed to be correct then 25 per cent of the F^{18} activity should be transferred to BF_3 on formation of the adduct, i.e. the same as obtained when BF_3^{18} is used for labelling the adduct.

If it is assumed that $SF_4^{18}.BF_3$ has one of the structures involving bridging fluorine atom (Fig.10), the probability of forming a F^{18} bridge is 25 per cent because in SF_4^{18} one fluorine atom out of four is expected to be radioactive. Assuming that the bridge bonds B-F and S-F are of comparable strength and the bridge is broken symmetrically then on decomposing the complex 12.5 per cent of the F^{18} activity would be transferred to BF_3 and the exchange would be expected to be independent of time.

The results of the exchange experiments on $SF_4^{18}.BF_3$ show that as the temperature is lowered the percentage of F^{18} exchange between SF_4^{18} and BF_3 decreased and reached a low value at -80° which fluctuated between 9 - 11 per cent (Table 15). These results naturally support the conclusion arrived at earlier.

The tracer study with F^{18} strongly favours a fluorine bridge covalent structure but it does not differentiate between the alternative structures shown in Fig. 10. To decide between these structures an X-ray diffraction study will almost certainly be necessary. A powder photograph could easily be taken, but it is unlikely to give any detailed information about the structure. It should be mentioned that the X-ray diffraction pattern of $SeF_4.BF_3$ 136).

which is analogous to $SF_4.BF_3$, could not be indexed most probably due to the low symmetry of its unit cell. The complex $SF_4.BF_3$ appears to be insoluble in all solvents except HF[134)] and the preparation of a single cyrstal of $SF_4.BF_3$ from HF solution or by sublimation has not yet been attempted.

Infra Red-Spectrum of Solid $SF_4.BF_3$, SF_4 and BF_3

The infra-red spectrum of $SF_4.BF_3$ reported by Seel and Detmer[27)] was observed between 600 and 1500 cm^{-1}, using NaCℓ window. They did not report the technique of sample preparation and the temperature at which the spectrum was taken. Therefore, the infra-red spectrum of $SF_4.BF_3$ was re-investigated at liquid air temperature. Maximum precautions were taken in the preparation of the adduct $SF_4.BF_3$ and the preparation of the sample for taking I.R. spectrum so as to eliminate all the chances of decomposition of the complex or formation of BF_4^- ion.

Preparation of $SF_4.BF_3$

A tube of about 100 mℓ capacity, fitted with a stop cock and a standard joint was connected to the vacuum line, evacuated and vacuum dried for about three hours. Then it was cooled in liquid air and equal volumes of purified SF_4 and BF_3 were condensed into it. The tube was slowly warmed to room temperature and allowed to stand for five to ten minutes. The complex $SF_4.BF_3$ was pumped for a short-time and then stored at liquid air temperature.

I. R. Sample Preparation

The 'Cold Finger' I. R. cell used in this work is shown in (Fig.14). The cell was connected to the vacuum line and pumped for about two hours. In order to remove traces of moisture which may remain adhering to the windows and the sample holder, the cell was filled with a little purified SF_4. After ten minutes the cell was pumped again for one hour. The plate holder was turned so that the plane of the centre plate was at right angles to the plane of the cell windows, and was facing the inlet tube. The stop cock 'S' (Fig.14) was closed and the centre plate 'P' on which $SF_4.BF_3$ was to be deposited was cooled to about -180° by pouring liquid air into A. It took about thirty minutes to cool the silver chloride plate and one hour to cool the polyethylene plate. About 100 mℓ of $SF_4.BF_3$ vapours at 2-5 mm pressure were introduced into the I.R. cell. As soon as the vapours came in contact with the plate a uniform thin layer of the compound $SF_4.BF_3$ was deposited. The stop cock 'S' was closed and the joint 'B' was warmed as quickly as possible with a fast current of compressed air and the plate holder was turned through 90°, so that the centre plate was parallel to the cell windows. Then liquid air was poured into 'A' to keep 'P' at about -180°. Solid samples of SF_4 and BF_3 were prepared similarly.

The infra-red absorption spectra of solid $SF_4.BF_3$, SF_4, and BF_3 were recorded between 250 cm^{-1} and 2100 cm^{-1}. The spectra of the compounds are shown in Fig.15 and the characteristic 1.R absorption frequencies are given in Table 16.

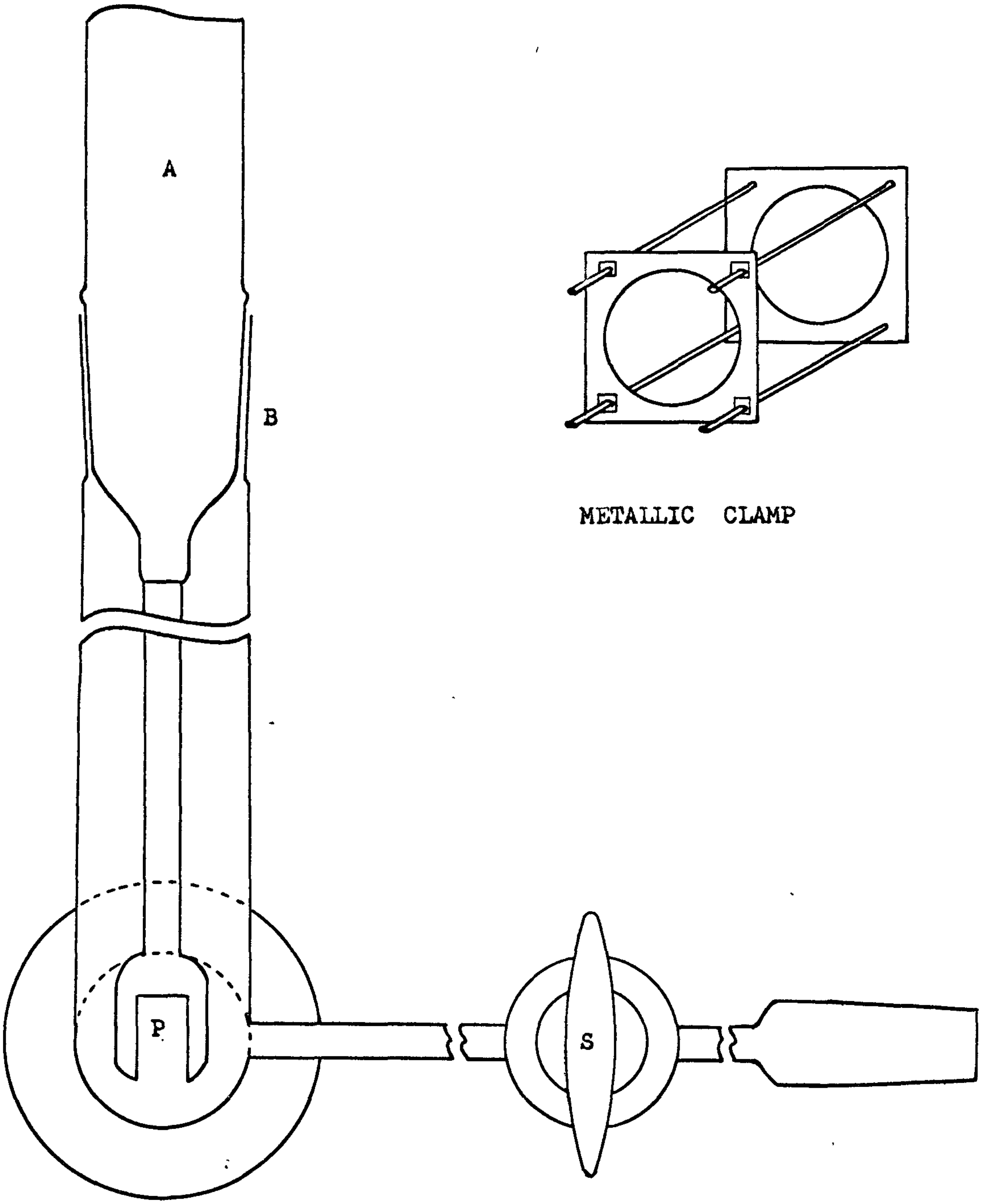


FIG.14 I.R. CELL

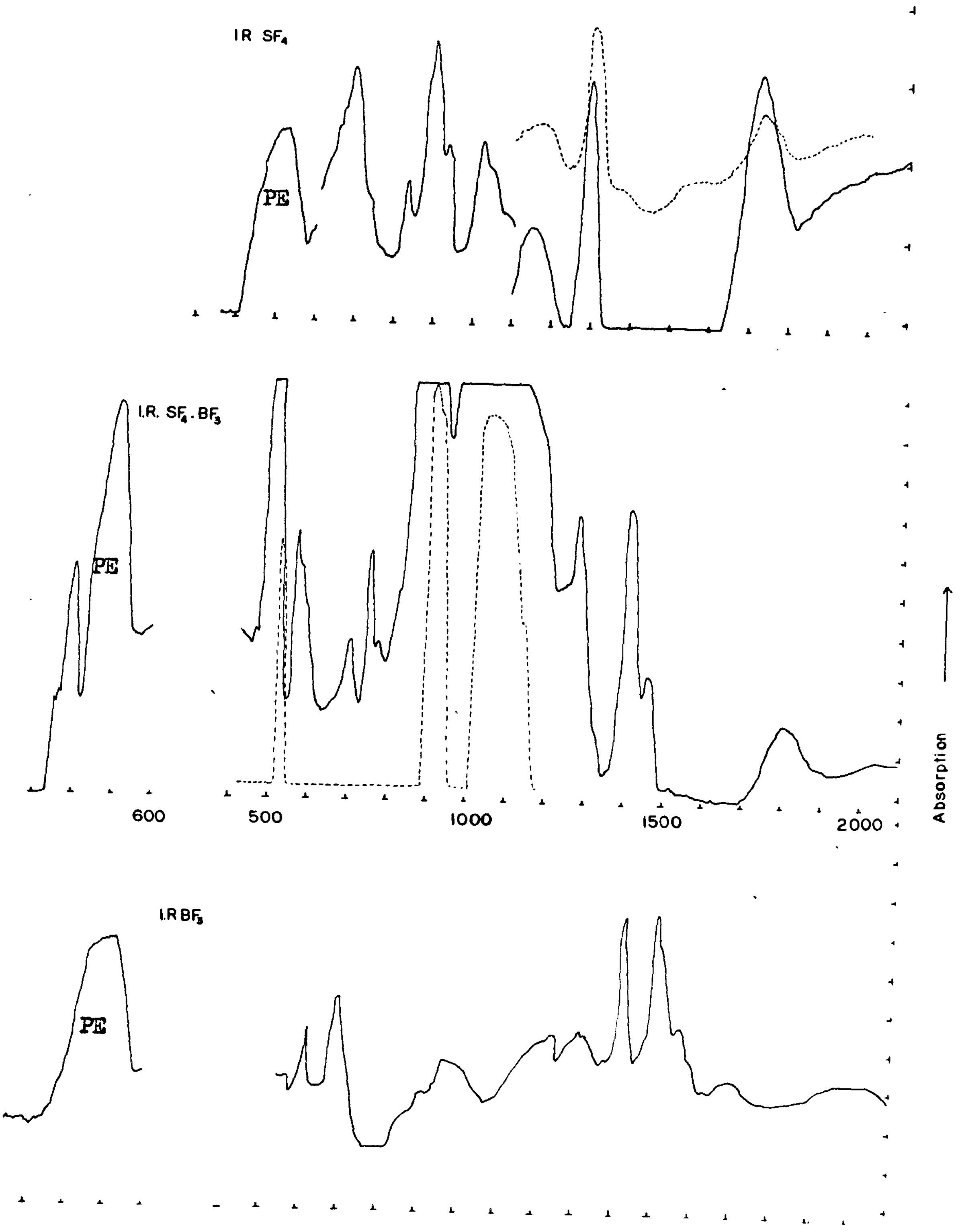


FIG 15

PE = Polyethylene Window

TABLE 16

Infra-Red Spectra of SF_4, $SF_4.BF_3$ and BF_3 Frequencies in cm^{-1}.

Gaseous SF_4 4)		Solid SF_4 (present work)	Solid $SF_4.BF_3$ (present work)	Solid BF_3	Gaseous BF_3 31,137)		
(1)		(2)	(3)	(4)	$B^{10}F_3$	$B^{11}F_3$	
235 (deduced)	ν_4		357 W				
463 V.W.	ν_4		370 W				
532 S	ν_7	505-520 S	409 m				
557 m	ν_3		465 W				
~ 645 (deduced)	ν_5 ?		518-523 V.S.	485 S	480S	482S	ν_4
715 m	ν_2 ?		532-538 V.S.	515S			
728 V.S.	ν_8	690 V.S.					
768		828 W	567 n				
867 V.S.	ν_6	880 V.S.	580 m	615 m			
889 V.S.	ν_1	890 V.S.	705 W	698S	691S	719S	ν_2
961 V.W.		930 m	753 m 773 m				
1070 V.W.		940 m	823 m	875 V.W.	888	888	ν_1
1091 W		1018 m	910 V.S.	900 W			

TABLE 16 (continued)

Infra-Red Spectra of SF_4, $SF_4.BF_3$ and BF_3^- Frequencies in cm^{-1}.

Gaseous SF_4 4) (1)	Solid SF_4 (present work) (2)	Solid $SF_4.BF_3$ (present work) (3)	Solid BF_3 (4)	Gaseous BF_3 31,137) $B^{10}F_3$	 $F^{11}F_3$
1098 W	1040 W	935 V.S.	965 S		
1114 W		1035-1090 V.S.			
1125 W	1150 m	1140 S			
1175 V.W.				1178 W	
1281 m. $\nu_8+\nu_3$	1290 S	1280 m	1238 m		
1369 V.W.		1330 V.W.	1310 m		
1421 W		1410 m.	1423 V.S.	1454 V.S.	1505 V.S. ν_3
1617 W		1460 W	1505 V.S.		
1678 V.W.			1564 m.		
1678 V.W.			1564 m.		
1710 V.W.			1685 W.		
1727 V.W.	1723 V.S.			1831 W.	
1744 m. $\nu_1+\nu_2$					
1778 V.W.		1805 W.			

s = strong
V.S. = very strong
m = medium
w = weak
V.W. = very weak

Discussion

The spectra of solid BF_3 and SF_4 have not been reported previously. The spectra of these compounds in the two phases, solid and gaseous appear to be similar (Table 16). The assignment of strong bands and fundamentals of gaseous SF_4 and BF_3 is given in Table 16. The weak lines are either overtones or combination lines. In the I.R. spectra of the two solids most of the weak lines were not observed. The I.R. frequencies of solid SF_4 and BF_3 have been assigned by comparing the I.R. spectra of the solids with those of the gaseous SF_4 and BF_3. The assignment is given in Table 17.

The intensity of some comparable bands in solid SF_4 is stronger than in gaseous SF_4, e.g. the intensity of the band at 1281 cm^{-1} in gaseous SF_4 is medium while the corresponding band at 1290 cm^{-1} in solid SF_4 is strong. In the I.R. spectrum of solid BF_3 the weak band at 875 to 900 cm^{-1} has been assigned to ν_1 although ν_1 is inactive in infra-red137). The appearance of ν_1 can be explained by assuming a weak intermolecular interaction in solid BF_3.

The infra-red spectrum of $SF_4.BF_3$ is different from that of solid SF_4 and solid BF_3 (Table 16; Fig.15). For example the prominent vibrational frequencies of solid SF_4, 880, 890 and 1723 cm^{-1} are not present in the spectrum of $SF_4.BF_3$; the same is true for some of the prominent frequencies of solid BF_3, e.g. 965, 1505 and 1564 cm^{-1}. The frequencies which are common between $SF_4.BF_3$ and SF_4 and/or BF_3 (Table 16, columns 2, 3 and 4), differ in intensity, e.g. the band in the region 515 - 525 cm^{-1} is present in all

TABLE 17

Assignment of Frequencies of Solid SF_4 and BF_3

SF_4 (cm^{-1})	BF_3 (cm^{-1})	Assignment
890	875 and 900	ν_1
	615 and 698	ν_2
505 - 520	1423 and 1505	ν_3
	485 and 515	ν_4
		ν_5
880		ν_6
505 - 520		ν_7
690		ν_8
		ν_9
1150		$\nu_1 + \nu_4$
1723		$\nu_1 + \nu_6$
930		$\nu_2 + \nu_4$
1290		$\nu_3 + \nu_8$
1040		$\nu_3 + \nu_9$
940		$\nu_4 + \nu_8$
1018		$\nu_7 + \nu_9$
828		?
	1564	?
	1681	?
	1238 and 1310	$2\nu_2$
	965	$2\nu_4$

the three spectra, but this band is very strong in the case of $SF_4.BF_3$, which indicates that this frequency is due to some species other than SF_4 or BF_3. New frequencies appear in the spectrum of $SF_4.BF_3$ at 357, 370, 409, 567, 580, 753 and 773 cm^{-1}, which are not present in either of the components. It is, therefore, evident that the spectrum No.2 (Table 16) is not due to a mixture of SF_4 and BF_3. The bands at 753, 773 and 935 cm^{-1} have also been confirmed in the Raman spectrum of $SF_4.BF_3$ 138).

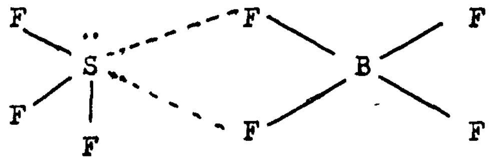
The ionic formulation, $SF_3^+ . BF_4^-$, of the complex does not account for all the lines in the infra-red spectrum (Table 16). In the tetrahedral BF_4^- ion only ν_3 and ν_4 are infra-red active and have been assigned previously at 1030 and 1060 cm^{-1}, and 520 and 535 cm^{-1} respectively (Table 18), the splitting being due to B^{10} and B^{11}. All the reported frequencies of BF_4^- ion are given in Table 18. The ion SF_3^+ being pyramidal (C_{3v}) can have four fundamentals, all infra-red active. The possible frequencies of SF_3^+ in the $SF_4.BF_3$ spectrum can be selected by comparison with the observed frequencies for PF_3 (Table 18) which is isoelectronic with SF_3^+. Due to the positive change on the sulphur atom the S-F bonds of SF_3 will be stronger than the P-F bonds of PF_3, therefore, the vibrational frequencies of SF_3^+ would be expected to be somewhat higher than those of PF_3. The frequencies at 1045 and 1055 cm^{-1}, and 532 and 538 cm^{-1} (Table 18) can be assigned to the BF_4^- ion and the lines at 935, 910, 518-523 and 370 cm^{-1} can be assigned to SF_3^+. However, many lines remain unassigned and the ionic model does not appear to account for the spectrum in a completely satisfactory manner.

TABLE 18

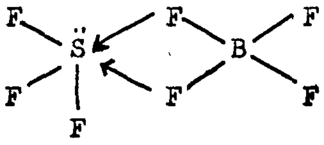
Vibrational Frequencies of BF_4^- and PF_3 in cm^{-1}

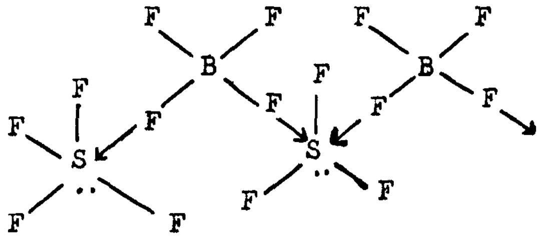
$SeF_4.BF_3$	$(CH_3)_3$ Sn BF_4		KBF_4		$NaBF_4$	NH_4BF_4	CH_3COBF_4			PF_3
135)	139)	140)	141)	142)	141)	141)	143)	144)	145)	137)
305	446	447								344
345	512									487
475	525	520	521	525	516	520	519			
519			535	536	527	533	537			
625										
746	746	758	772	733	779	766		786	769	860
1000	930									
1056	1070	1100	1030	1038	1036	1030	1052		1026	892
1080	1115		1059	1063		1063			1064	
	1170			1078 1088	1078					
	1200		1290	1107 1128		1289		1100		
			1305	1312 1623 1644 1671 2340 2925	1305	1300	1293		1300 1529	

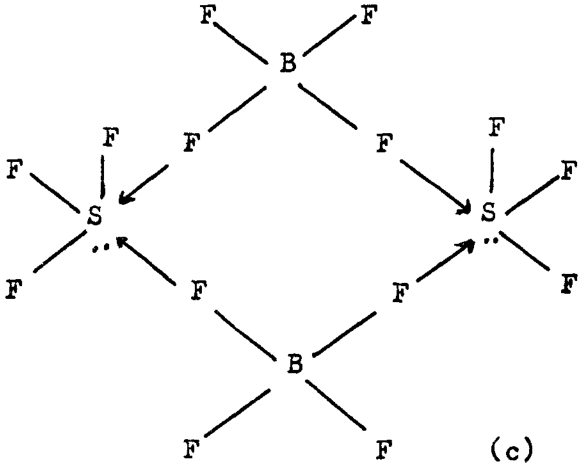
If the solid $SF_4.BF_3$ consists of SF_3^+ and BF_4^- the two ions would be expected to interact through fluorine. It is, therefore, possible to envisage a semi-ionic or ion-pair case in which there are fluorine bridges. Such as:



In the limit this interaction would approach closely covalent bonding between the two groups to give one of the following structures:


(a)


(b)


(c)

The above mentioned fluorine bridged structures of $SF_4.BF_3$ are essentially the same as shown in Fig.10. Thus the fluorine bridged structure of

$SF_4.BF_3$ may be regarded as arising from strong interaction between the two ions.

For the sake of simplicity interactions between SF_3^+ and BF_4^- will be considered. Interaction between the ions can reduce the site symmetry of BF_4^- to C_{3v} (interactions at one fluorine) or C_{2v} (interaction at two fluorine). The degeneracy is only partially removed in C_{3v}, but is completely removed under C_{2v} symmetry. The strong band in the region 1030 - 1200 cm^{-1} shows two maxima at 1045 and 1085 cm^{-1} and a shoulder at 1140 cm^{-1} which is possible if the degeneracy is completely removed. Further splitting observed may be due to the isotopic shift. This assignment agrees with that of Whitla[136)] for BF_4^- in $SeF_4.BF_3$ and that of Clark and O'Brien[139)] for BF_4^- in $(CH_3)_3$ $SnBF_4$ where C_{2v} site symmetry for the BF_4^- ion has been reported. The BF_4^- under C_{2v} symmetry would be expected to have nine fundamentals[136,146)]. The frequencies that can be assigned to BF_4^- in $SF_4.BF_3$ are given in Table 19.

The symmetry of SF_3^+ by analogy with PF_3[137)] would be expected to be C_{3v}, in which all the four fundamentals are infra-red active. Due to interaction between the ions the site symmetry of SF_3^+ may be reduced to C_{2v} or C_s; in either case all the degeneracies will be removed. Therefore, SF_3^+ would be expected to have six fundamentals, all infra-red active[137,146)]. The frequencies assigned to SF_3^+ are given in Table 19. By comparison with the S-O asymmetric stretch in the SOS group[187)] the frequency at 773 cm^{-1} can be assigned to the asymmetric S-F stretch in the fluorine bridge. The other fluorine bridge frequencies are likely to be of much lower frequency occur below 250 cm^{-1}. The frequencies above 1300 cm^{-1} have been

TABLE 19

Assignment of Frequencies (cm^{-1}) of SF_3^+ and BF_4^- in $SF_4.BF_3$

BF_4^-	SF_3^+	Assignment
1085 (1035-1090)	935	ν_1
753	910	ν_2
409	520	ν_3
535	370	ν_4
357	823	ν_5
1140	357	ν_6
578		ν_7
1050 (1035-1090)		ν_8
465		ν_9
1330		$\nu_2 + \nu_7$
1410		$\nu_4 + \nu_8$
1460		$\nu_1 + \nu_5$
	1805	$2\nu_2$

assigned to combination lines or overtones(Table 19). Thus all the I.R. frequencies of $SF_4.BF_3$ can be satisfactorily accounted for on the basis of the covalent structure of $SF_4.BF_3$ (Fig.10).

It is not possible to distinguish between the structures shown in Fig.10.

F^{19} NMR Spectrum of $SF_4.BF_3$ Solution in HF.

The fluorine nuclear magnetic resonance spectrometric technique has not been used so far for investigating the structure of $SF_4.BF_3$ probably because no suitable solvent could be found. However, it has been found that $SF_4.BF_3$ dissolves in anhydrous HF134) without apparent decomposition. Therefore, the fluorine NMR spectrum of a solution of $SF_4.BF_3$ in HF was investigated.

Preparation of $SF_4.BF_3$ - HF Sample

A Keℓ-F tube about 22 cm long and 4 mm across was taken. One end of the tube was heat sealed and the other end made into a flange. The tube was connected to a NUPRO polyethylene valve (Catalogue N-860, Nuclear Products Company, 15635 Sanarác Road, Cleveland, 10, Ohio, U. S. A.) through a monnel metal adapter, as shown in Fig.16. The assembly was connected to the vacuum line and evacuated for about thirty minutes. In order to remove traces of moisture, the tube was filled with a little purified SF_4 and pumped again for one hour. Then the Keℓ-F tube was cooled in liquid air and vapours of purified $SF_4.BF_3$ were condensed into it. ($SF_4.BF_3$ was prepared and purified in the same way as for the measurement of its

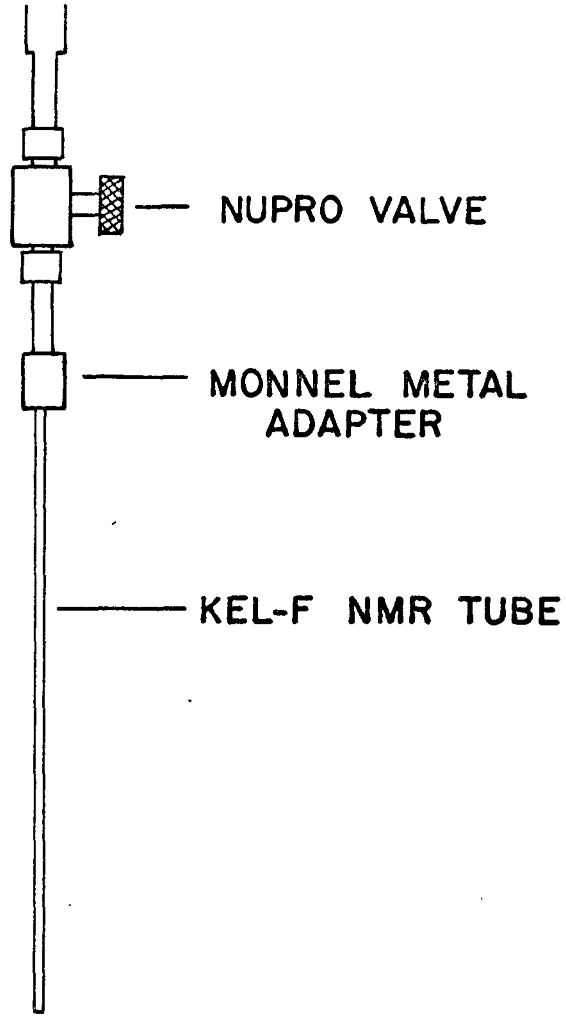


FIG. 16

infra red spectrum). It was then connected to the HF line, pumped and HF was condensed in the Keℓ-F-tube. Then the Keℓ-F NMR tube was heat sealed at the top and inserted into a thin walled pyrex NMR tube. A homogeneous solution was obtained on warming the tube to room temperature.

The NMR spectra of the SF_4-HF, BF_3-HF, $SF_4.AsF_5$-HF and AsF_5-HF systems were also observed between room temperature and -110°. The spectra of these compounds are also discussed here because they are relevant to the interpretation of the $SF_4.BF_3$ spectra.

Preparation of $SF_4.AsF_5$-HF, SF_4-HF, BF_3-HF and AsF_5-HF Samples

The complex $SF_4.AsF_5$ could not be condensed into the Keℓ-F NMR tube because it has a very small vapour pressure at room temperature25) and it was, therefore, prepared directly in the NMR tube. Equal volumes of SF_4 and AsF_5 were condensed into the NMR tube, cooled in liquid air and the tube was then slowly warmed to -70°. After the reaction was over the tube was pumped for a short time to remove any unreacted components. A suitable amount of HF was condensed into the tube, which was then heat sealed at the top and inserted into a standard thin walled pyrex NMR sample tube. When the tube was warmed a yellowish solution was obtained which solidified at -50°.

The samples of SF_4 - HF, BF_3 - HF and AsF_5 - HF were prepared in the same way as the $SF_4.BF_3$ - HF sample. In all the cases homogeneous solutions were obtained even at -110°. The AsF_5 solution had a faint green colour, but the other two were colourless.

F^{19} NMR Spectra

$SF_4.BF_3$ - HF. At room temperature the NMR spectrum of $SF_4.BF_3$ - HF consisted of a very broad peak. As the temperature was lowered this peak gradually narrowed. At -15° another broad peak appeared down field from the broad peak. The number of fluorine signals remained unchanged down to -110°, but both peaks became sharper and the intensity of the signal at low field increased. The NMR spectra of the $SF_4.BF_3$ - HF system at various temperatures are shown in Fig.17. The chemical shifts and peak widths of F^{19} resonance signals of the $SF_4.BF_3$ - HF system with respect to HF are given in Tables 20 and 21.

$SF_4.AsF_5$ - HF. The sample froze at -50°, therefore, the F^{19} spectrum was taken at room temperature, -30° and -45°. At room temperature no fluorine-19 resonance signal was observed. At about 0° a very broad signal appeared. As the temperature was lowered the width of the signal decreased and at about -25° a second small signal appeared down field from the broad peak, which became sharp and prominent at -30°. Both signals could be observed down to -48°. As the temperature was lowered the widths of the signals decreased and their amplitude increased. At -50° the peak at low field gradually faded, but the high field resonance signal was observed down to -70°. The spectra at different temperatures are shown in Fig.18. The chemical shifts and the peak widths of the signal are given in Tables 20 and 21.

BF_3 - HF. The F^{19} NMR spectrum was observed at -110° and -80°. At each temperature only one signal was obtained, the width of the signal was inversely related to the temperature (Table 20).

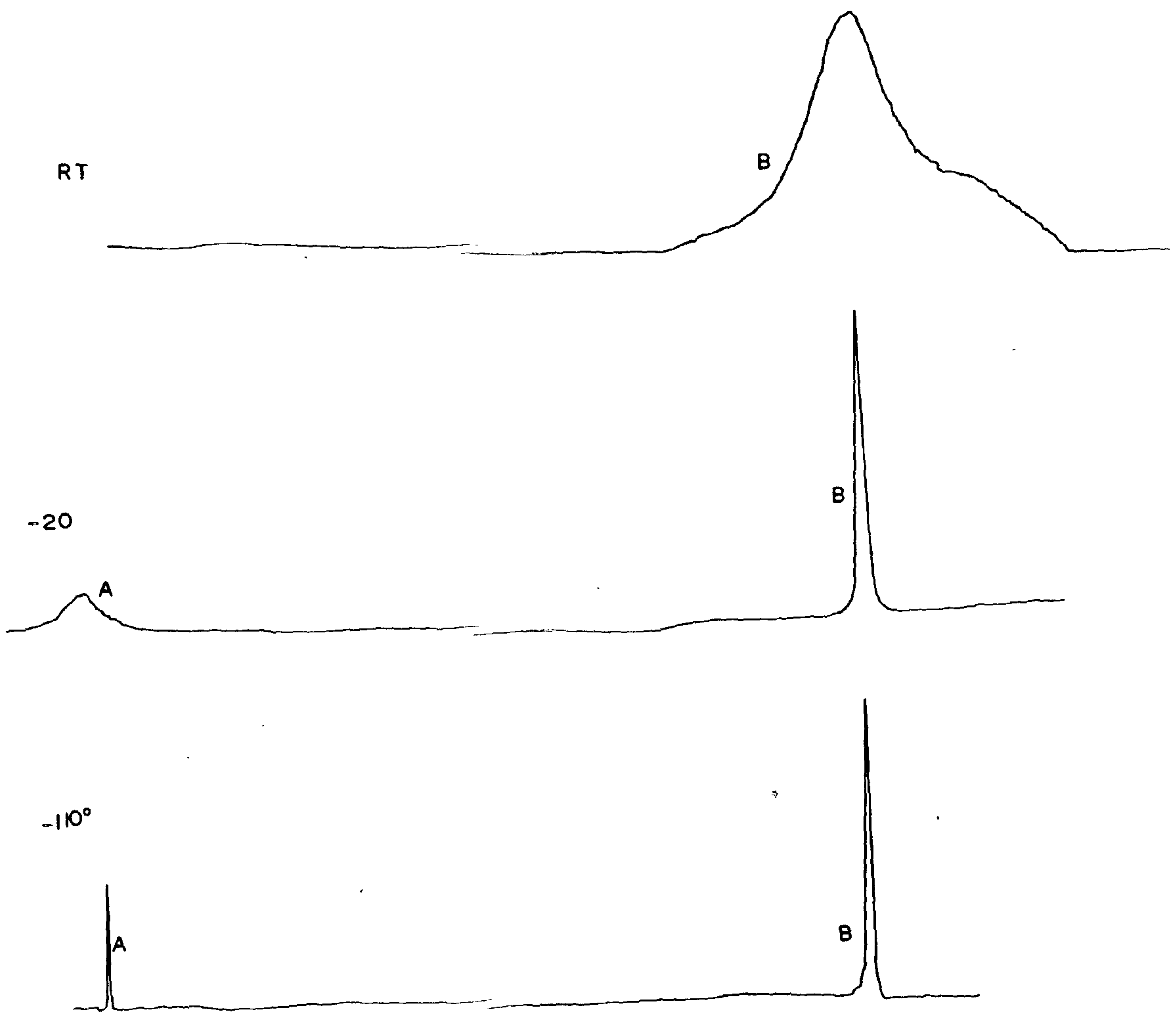
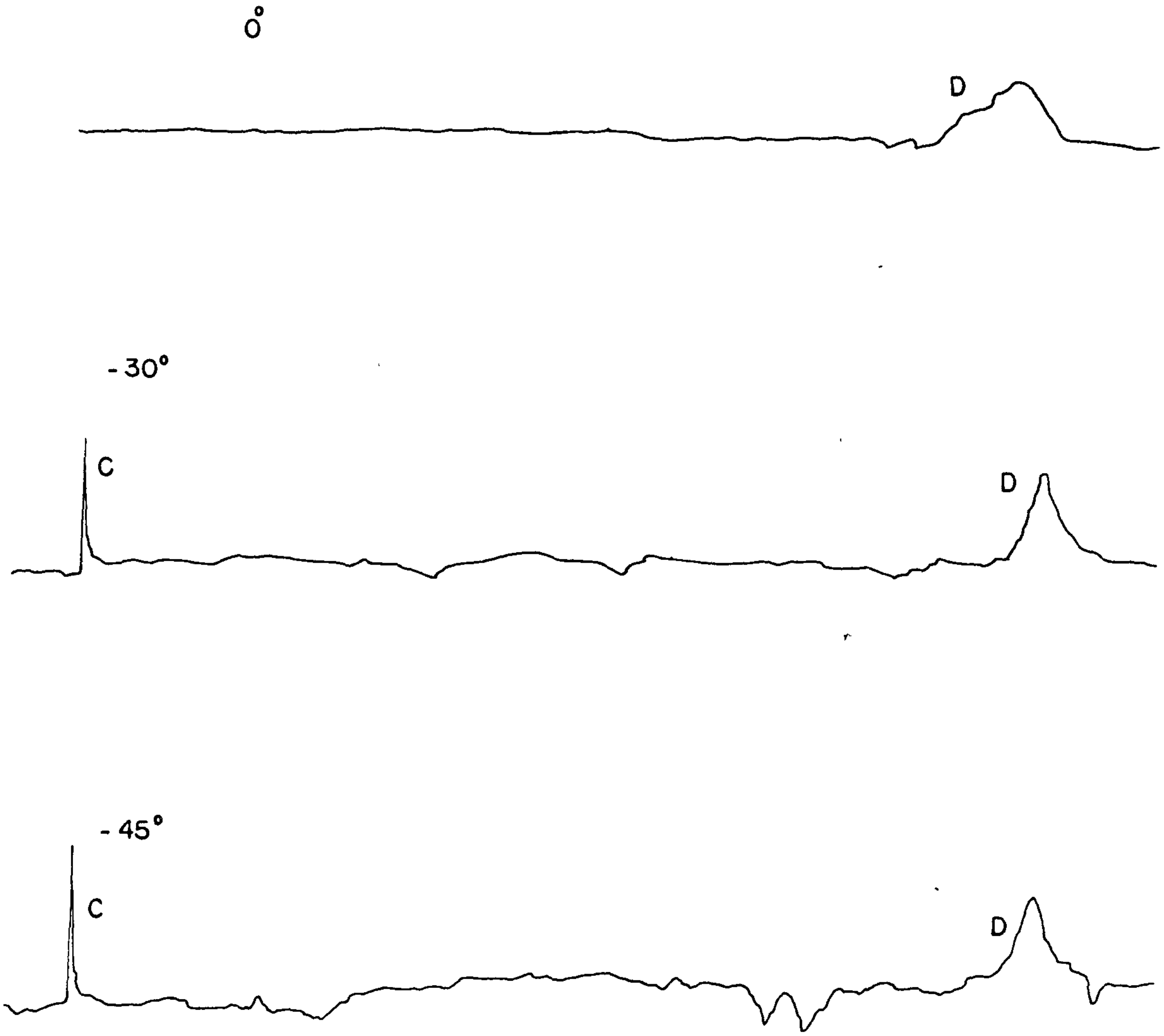


FIG 17 F^{19} NMR OF $SF_4 \cdot BF_3$—HF



FIG·18·F^{19} NMR OF $SF_4 \cdot AsF_5$— HF

SF_4 - HF The F^{19} NMR spectrum was observed between -30° and -110°. The spectrum consisted of a single broad peak at all temperatures (Table 21).

AsF_5 - HF The F^{19} NMR spectrum was observed between room temperature and -115°. At room temperature the spectrum consisted of a single broad peak. At -30° the signal became broad at the base and at -60° it split up into two partially overlapping peaks, one tall and the other short (Fig.19). The appearance of the signal did not change down to -110°. At -110° the two signal coalesced. At about -118° the signal gradually faded away indicating that the sample had frozen. The chemical shifts and the peak widths are given in Tables 20 and 21.

Discussion

At ambient temperature the $SF_4.BF_3$ solution gave one F^{19} resonance signal (B) at a very high field. The half width of B at room temperature was 1440 cps. At low temperatures the signal B became narrow and another signal A appeared down field from B (Fig.17). The separation between the two signals was between 224.4 ppm and 215 ppm depending upon the temperature. The chemical shift of B with respect to HF was between -8.8 ppm and -8.4 ppm (Table 20).

Because of the large separation between A and B it is likely that the two resonance signals are due to fluorine atoms attached to nuclei of two different elements. Therefore, it is suggested that the complex $SF_4.BF_3$ may dissolve in HF according to one of the following mechanisms

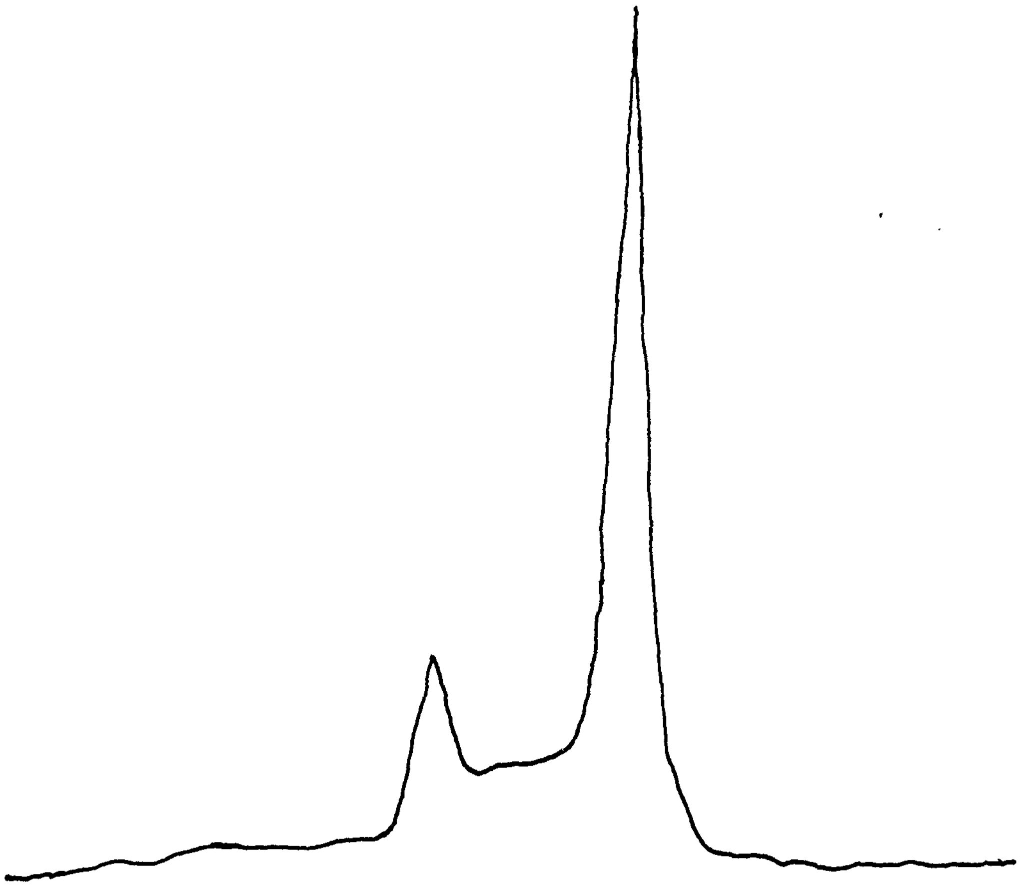


FIG. 19 F^{19} NMR Spectrum of AsF_5-HF

TABLE 20

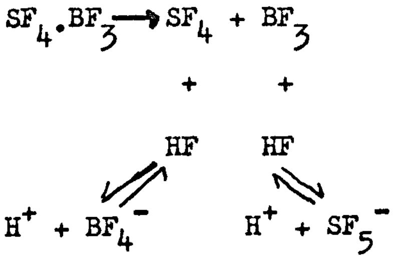
Chemical Shifts of $SF_4.BF_3$ - HF, SF_4AsF_5 - HF, SF_4 - HF, SF_3 - HF in parts per million (ppm) and AsF_5 - HF signals with respect to HF

Temperature	SF_4 BF_3 - HF		SF_4 AsF_5 - HF				
	Low Field Peak (A)	High Field Peak (B)	Low Field Peak (C)	High Field Peak (D)	SF_4 - HF	BF_3 - HF	AsF_5 - HF
R.T.	-	-	-	-	-	-	-
-15°	-233.2	-8.8	-	-	-	-	-
-30°	-225.6	-8.4	-223.6	-5.3	-	-	-20.5
-45°	-	-	-223.9	-3.2	-	-	-
-60°	-223.5	-8.4	-	-2.7(70°)	-88.1	-	-26.8
-80°	-	-	-	-	-	-6.8	-
-90°	-222.8	-8.4	-	-	-87.9	-6.8	-28.4

TABLE 21

Width of $SF_4.BF_3$ - HF, SF_4AsF_5 - HF, SF_4 - HF, BF_3 - HF and AsF_5 - HF Signals at half maximum in cycles per second cps.

Temperature	$SF_4.BF_3$ - HF		SF_4AsF_5 - HF		SF_4 - HF	BF_3 - HF	AsF_5 - HF	
	A	B	C	D			Half width of the tall peak	Separation of tall peak from the
R.T.	-	114	-	-	-	-	31.0	-
-15	852.6	230	-	1165	-	-	-	-
-30	423.5	70	39.6	1024	51.6	-	75	-
-45	-	-	19.3	780	-	-	-	-
-60	9.4	33.4	-	-	63.9	-	33.1	196.8
-80	-	-	-	57.8	-	35.4	-	-
-90	-	-	-	-	-	-	34.3	187.3
-100	-	-	-	-	-	-	57.8	181
-110	3.5	20.4	-	-	38.0	51.9	83.0	
-115	-	-	-	-	-	-	125.0	-

(i) 

(ii) $$SF_4.BF_3 \overset{HF}{\rightleftharpoons} SF_3^+ + BF_4^-$$

The chemical shift of the SF_4 - HF signal with respect to HF was between 87.9 and 88.1 ppm (Table 20) and the calculated chemical shift of the SF_4 signal at room temperature with respect to HF is -260.3 ppm. The fact that the chemical shift of A,- 233.2 to -222.8 ppm, (Table 20) lies between the chemical shifts of SF_4 and SF_4 - HF indicates that the signal A was probably due to fluorine on sulphur.

Sulphur tetrafluoride is known to be a F^- ion acceptor$^{22)}$ therefore, in the hydrofluoric acid solution of SF_4, exchange of fluorine may occur via the equilibrium

$$HF + SF_4 \rightleftharpoons HSF_5 \rightleftharpoons H^+ + SF_5^- \qquad (3)$$

The fact that the SF_4 - HF solution displayed one signal at all temperatures indicates that fluorine exchanges rapidly between SF_4 and HF probably by the above mechanism. The chemical shift of the SF_4 - HF signal would be expected to depend upon the concentration of SF_4 and it would move towards the HF resonance, as the concentration of SF_4 is decreased.

A comparison of the F^{19} resonance spectra of $SF_4.BF_3$ - HF and $SF_4.AsF_5$ - HF shows that the chemical shifts of A and C are almost the same. Had these two signals 'A' and 'C' been due to SF_4 exchanging with HF the chemical shifts of 'A' and 'C' would not be expected to be so close unless by sheer coincidence the molar concentration of $SF_4.BF_3$ in HF was the same as that of $SF_4.AsF_5$. The proximity of A and C indicates that most probably they are due to the same fluorine species. Another distinctive feature of A and C is their sharpness at low temperatures (Table 21) which suggests that all the fluorines on the sulphur atom are equivalent, which would be the case in SF_3^+, and at low temperatures the fluorine exchange between HF and SF_3^+ had become slow.

In SF_4 the equatorial and axial S-F bond are formed by sp^2 and pd_{z^2} hybrid orbitals7,15) respectively. In the SF_3^+ ion the bond would be expected to be formed by sp^3 hybrid orbitals. Therefore, the S-F bond length in SF_3^+ would be expected to be close to the S-F distance (equatorial). The fluorine resonance signal of SF_4 displays two triplets at low temperatures5,6). It would be logical to assume that the triplet at high field could be due to the equatorial fluorines. Therefore, it would be expected that the F^{19} resonance signal due to SF_3^+ would occur close to the high field triplet of SF_4. It has been calculated that the chemical shift of the high field triplet with respect to HF is -233.4 ppm, comparable with that of signal A (Fig.20). Thus the signal A is most probably due to SF_3^+.

The evidence cited above favours mechamism (ii) for the dissolution of $SF_4.BF_3$ in HF. Therefore, the signal 'B' in the spectrum of $SF_4.BF_3$ would be expected to be due to fluorine exchanging between BF_4^- and HF. The conclusion regarding the BF_4^- ion exchanging with HF could be confirmed by observing the spectrum of $SF_4.BF_3$ solution containing $NaBF_4$ or KBF_4. The spectrum would be expected not to show any additional resonance signal, but the intensity of the signal B would be increased.

In the $SF_4.AsF_5$ - HF spectrum, taken at -30° and -45°, two signals were observed. The low field peak C was considered to be due to SF_3^+ because of the proximity of the chemical shifts of A and C (Table 20). By analogy with the signal B of $SF_4.BF_3$ the high field peak D was considered to be due to AsF_6^- and HF, a single peak being observed because of rapid fluorine exchange. It is, therefore, concluded that in HF solution the complex of SF_4 with a Lewis acid such as BF_3, AsF_5, etc. is ionized into SF_3^+ and the corresponding anion.

At room temperature, due to rapid exchange of fluorine between HF, BF_4^- and SF_3^+ in the $SF_4.BF_3$ solution, the signal B had become broad and the signal A had become so broad that it could not be observed.

The chemical shift of F^{19} resonance signal from BF_3 - HF was found to be -6.8 ppm with respect to HF. The signal B was close to this resonance. It was, therefore, inferred that even at -80° and below BF_3 and HF exchange fluorine via BF_4^-. The chemical shift between B and the BF_3 - HF system may be attributed to the different strengths of the two solutions with respect to BF_3.

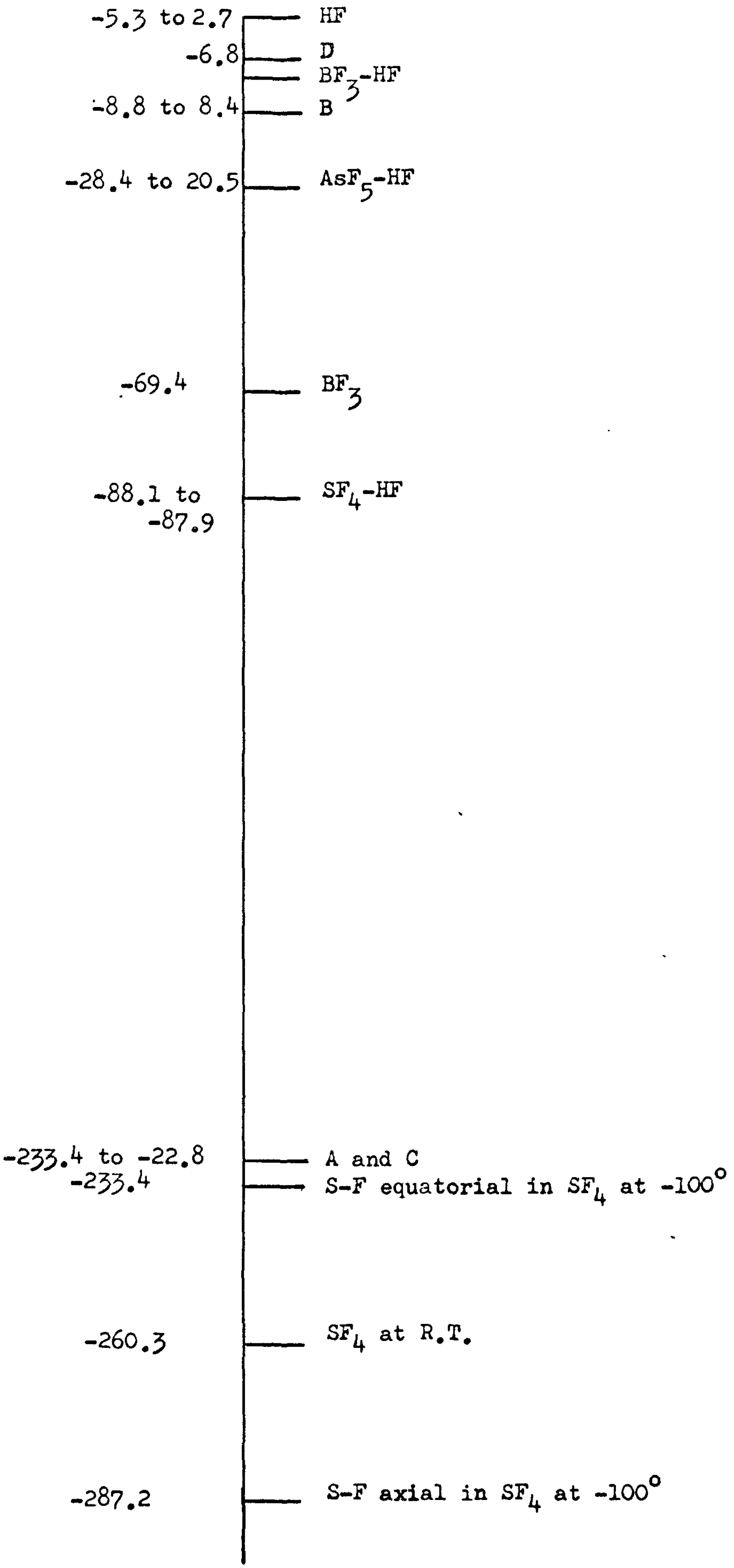


FIG.20 REPRESENTATIVE CHEMICAL SHIFTS IN VARIOUS FLUORIDES FOR F^{19} - ppm.

It has been reported by MacLean and MacKor147) that at -75° the F^{19} resonance signal of BF_3 - HF containing some water displayed a well defined quadruplet structure due to BF_4^-, whose chemical shift with respect to HF was found to be -41.75 ppm. The splitting of the BF_4^- signal is due to spin-spin coupling between fluorine and B^{11} ($I = 3/2$). This shows the BF_4^- does not exchange fluorine with HF under these conditions. Anhydrous $HBF_4$148) has not been obtained, although aqueous solutions containing 80 to 85 per cent of the material have been prepared. It is well known that aqueous HBF_4 is a strong acid and it does not contain free HF. These facts lead one to conclude that relatively small amounts of water stabilizes HBF_4. Therefore, the absence of structure in the signal 'B' seems to be due to extremely fast exchange fluorine between HF and BF_4^-.

At room temperature, due to rapid exchange of fluorine between HF, SF_3^+ & AsF_6^- the signals C and D had flattened out and could not be observed. However, at about 0° a very broad signal 'D' became narrow as the temperature was lowered. At -30° and -45° the chemical shift of 'D' was found to vary from -5.3 and -3.2 ppm. By analogy with the signal 'A' of $SF_4.BF_3$ - HF, signal 'D' may be assumed to be due to the fluorine rapidly exchanging between HF and AsF_6^-. The preceding conclusion is also supported by the fact that the formation of SF_3^+ and AsF_6^- by the ionization of $SF_4.AsF_5$ is highly probable because AsF_5 is a stronger Lewis acid than BF_3.

The solution of $SF_4.AsF_5$ froze at about -50°, but the signal 'D' could be observed even at -70°. The chemical shift of D at -70° was

-2.7 ppm. This observation may be explained by assuming that below -50° excess HF did not solidify and it contained a little dissolved SF_3^+ AsF_6^-. Thus D was essentially due to AsF_6^- - HF. The SF_3^+ signal could not be observed probably due to its very small concentration.

Arsenic pentafluoride would be expected to exchange fluorine with HF, via AsF_6^- 13). The chemical shift of the AsF_5 - HF signal with respect to HF was temperature dependent and it varied between -28.4 and -20.4 ppm. Moreover the AsF_5 - HF signal (Fig.19) was composed of two partially overlapping peaks between -110° and -40° and at any temperature it was not as wide as the signal D. The chemical shifts of D and the F^{19} resonance of AsF_5 - HF could be due to the different concentrations of AsF_5 in the solutions. The shape of the AsF_5 - HF spectrum could not be explained on the basis of the present data. In order to obtain complete understanding of the SF_4 - HF and AsF_5 - HF systems further measurements are needed.

Conclusion

The evidence obtained from the tracer study and infra-red spectroscopy of solid $SF_4.BF_3$ favours one of the covalent structures involving bridging fluorine atoms.

The evidence obtained from the F^{19} NMR investigation favours the formation of SF_3^+ and BF_4^- when the complex $SF_4.BF_3$ is dissolved in anhydrous HF. Similar behaviour was shown by $SF_4.AsF_5$. It would be expected that the other complexes of this series viz: $SF_4.PF_5$, $SF_4.SbF_5$

etc. would dissolve in HF producing the proposed SF_3^+ and the corresponding anions.

Further confirmation of the ionization of the SF_4 complexes in HF could be obtained by determining the conductivities of these solutions.

CHAPTER 6

F^{18} Exchange Reactions of SF_4 with the IVB and VB Group Covalent Fluorides

In this chapter the exchange of F^{18} between SF_4 and other covalent fluorides viz: PF_5, AsF_5 and SiF_4 will be discussed. Sulphur tetrafluoride forms 1:1 adducts with PF_5 26) and AsF_5 23-26). Muettertie s et al. 17) have reported that SF_4 does not interact with SiF_4 although $(SF_4)_2.GeF_4$ is known 17,26).

$SF_4.PF_5$ and $SF_4.AsF_5$

The properties and stereochemistry of PF_5 and AsF_5 are similar, therefore, their exchange reactions will be described together. Bartlett and Robinson 25) have stated that $SF_4.AsF_5$ is more troublesome to prepare than $SF_4.BF_3$. In the present investigation no such difficulty was encountered, rather in both cases the synthetic reaction proceeded smoothly.

The adduct $SF_4.AsF_5$ has been described as highly reactive towards diethyl ether 25), but the reaction products have not been mentioned. It is known that AsF_5 is extremely reactive towards even very weak organic bases 9,46). Therefore, it would be expected that ether would displace SF_4 from $SF_4.AsF_5$ (cf. $SF_4.BF_3$). Phosphorus pentafluoride is almost identical with AsF_5 in its chemical properties, therefore, a similar reaction between ether and $SF_4.PF_5$ would be expected.

The above reaction of $SF_4.AsF_5$ and $SF_4.PF_5$ with ether was verified in the following manner. The adducts $SF_4.PF_5$ and $SF_4.AsF_5$ were made by condensing equal volumes of the constituent fluorides at liquid air temperature followed by warming to room temperature. As soon as SF_4 melted a vigorous reaction ensued. The complexes thus formed were pumped for a short time to remove any unreacted components. When dry ether was added to the complexes at room temperature, an exothermic reaction took place and the organic component was charred. The reaction between the adducts and ether was then observed at low temperature. When ether (cooled to -80°) was added to the complexes maintained at -80°, no visible change was observed. When the reactants were warmed to -50° a slow reaction was observed which became rapid on warming to -40°. The gaseous product of the reaction was collected in a receiver and was found to be SF_4. The solution of the products in excess of ether was colourless initially, but became pale after about thirty minutes. The intensity of the colour increased with time.

Exchange of F^{18} between XF_5^{18} and SF_4 on the formation of the adduct $SF_4 . XF_5^{18}$

The pentafluorides (PF_5 and AsF_5) were labelled with F^{18} as described in Chapter 3. The apparatus and the experimental arrangements employed for studying the exchange reaction were the same as described for $SF_4.BF_3$ (Chapter 5). Equal volumes of purified SF_4 and the labelled pentafluoride were condensed in the reaction vessel D, (Fig.7), cooled in liquid air. The reaction vessel was then warmed to -130° in an n-pentane bath and the temperature was slowly raised until SF_4 melted. When the reaction between SF_4 and XF_5 had been completed the low temperature bath was warmed to -40°. The reaction vessel was pumped for a short time to remove the unreacted constituent and it was then maintained at -40° for thirty minutes. Then the reaction vessel was chilled in liquid air and 5 mℓ of dry ether, cooled to about -80°, were added to the adduct. The reaction vessel was again put in an n-pentane bath (-130°) and warmed slowly to -40°. The SF_4 displaced by ether was collected in the receiver E (Fig.7). The contents of the reaction vessel and the SF_4 were hydrolysed with ice-cold NaOH solution (16 per cent) and made up to 250 mℓ. The F^{18} activity in the solutions was measured as usual and solutions were analysed for SF_4 and XF_5.

In respective experiments the solutions containing displaced SF_4 were tested for AsO_4^{3-} with silver nitrate[128,132] or for PO_4^{3-} with ammonium molybdate reagent[128,132]. In each case the test was negative showing that the SF_4 fraction was not contaminated with the labelled pentafluoride.

The procedure employed for determining the specific activity of the labelled pentafluorides was the same as that of BF_3^{18}. The results are given in Table 22.

Discussion

The complexes $SF_4.PF_5$ and $SF_4.AsF_5$ can be represented by one of the following structures:

I $F_4S \rightarrow XF_5$ (X = P or As)

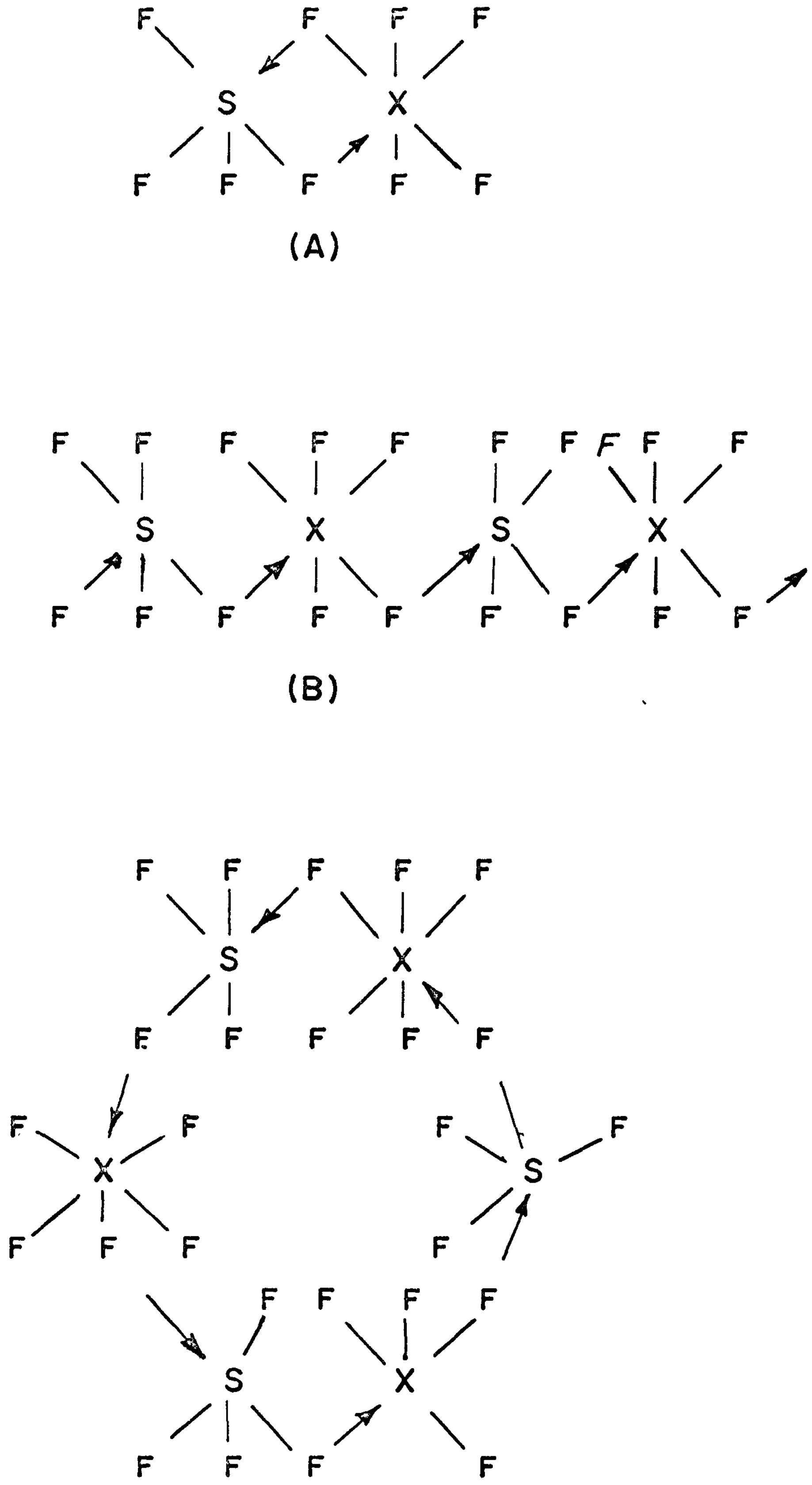
II $SF_3^+ \quad XF_6^-$

III Fluorine bridge structure (Fig.21) analogous to that proposed for $SF_4.BF_3$

TABLE 22

F^{18} Exchange between XF_5^{18} and SF_4 on the Formation of the adduct $SF_4.XF_5^{18}$

		$SF_4.PF_5$	$SF_4.AsF_5$
1.	Count min^{-1} g^{-1} for XF_5^{18} at zero time	62000	249000
2.	Weight in g. of XF_5 in the complex $SF_4.XF_5^{18}$	2.5798	1.2738
3.	Weight in g. of SF_4 in the complex	2.2027	0.8135
4.	Weight in g. of SF_4 separated	0.6647	0.10624
5.	Counts min^{-1} for SF_4 separated from $SF_4.XF_5^{18}$	12855	11980
6.	Counts min^{-1} for the residue	147200	320000
7.	Total activity of XF_5^{18} in the complex at zero time (sum of 5 and 6)	160055	331980
8.	Counts min^{-1} forXF_5^{18} in the complex at zero time (1 and 2)	1599476	3171762
9.	Total counts min^{-1} transferred to SF_4 at zero time (3, 4 and 5)	41600	91639
10.	Percentage activity transferred to SF_4 (7 and 9)	25.9	27.6



(A)

(B)

(C)

FIG:21

If the complexes involve a simple coordinate bond between the sulphur atom and the phosphorus or arsenic atom no exchange would be observed between the component fluorides of $SF_4.XF_5$ on decomposition of the adduct. Therefore, the above results definitely rule out the Lewis acid-Lewis base type structure for $SF_4.XF_5$. The F^{18} exchange would, however, be obtained on decomposition of either II or III.

Employing the same arguments as used for $SF_4.BF_3$ it can be shown that structure III would lead to a transfer of 10 per cent of the F^{18} activity from XF_5^{18} to SF_4, while II would lead to a transfer of 16.7 per cent of F^{18} activity. The reaction between XF_5 and SF_4 appears to be a lot more vigorous and exothermic than the reaction between SF_4 and BF_3. It is not conceivable that the heat of the reaction would be dissipated instantaneously from all parts of the complex. Therefore, certain portions of the compound would be subjected to localized heating for a short time, which might lead to localized exchange F^{18} via the dissociative mechanism. Thus there is finite probability that during the formation of $SF_4.XF_5$ more than the theoretical amount of F^{18} may be exchanged between SF_4 and XF_5. Furthermore, it does not seem practical to study the exchange rate at temperatures lower than -50° because below this temperature the complexes do not appear to react with ether. Thus from the results of the F^{18} tracer study no definite conclusion can be drawn either in favour of structure II or III.

SF_4 - SiF_4 System

The properties and stereochemistry of SiF_4 and GeF_4 are similar, therefore, SiF_4 would be expected to form a (1:2) adduct with

SF_4 as does the latter[17,26]. Muetterties et al.[17] found no evidence for complex formation or fast fluorine exchange within the temperature range -90° to +100°. They, however, found that the system $AsF_3 - SF_4$ gives one fluorine resonance signal down to -60°, indicating only one fluorine environment, which was attributed to a fast exchange. They were unable to explain the absence of interaction between SiF_4 and SF_4 in view of the fact that SiF_6^{2-} ion is very stable as compared to AsF_4^-. The $SiF_4 - SF_4$ system has, therefore, been re-investigated employing the following techniques:

(i) Exchange of F^{18} between SiF_4^{18} and SF_4;

(ii) Vapour pressure measurements of $SiF_4 - SF_4$ systems;

(iii) F^{19} NMR spectroscopy of $SiF_4 - SF_4$ mixtures;

(iv) Infra-red spectroscopy of (1:1) and (1:2) mixtures of SiF_4 and SF_4 at liquid air temperature.

Exchange of F^{18} between SiF_4^{18} and SF_4

The apparatus and the experimental procedure used in this investigation were the same as described under $SF_4.BF_3$. Silicon tetrafluoride was labelled with F^{18} by passing SiF_4 over LiF^{18} (Chapter 3).

In a separate experiment it was found that (1:1) and (1:2) mixtures of solid SiF_4 and SF_4 showed no sign of melting up to -55°, although the melting point of SF_4 is -121° and SiF_4 sublimes at -95.3°.

Equal volumes of purified SF_4 and SiF_4^{18} were condensed in the reaction vessel, cooled in liquid air. The reaction vessel was slowly warmed to -60° and maintained at this temperature for thirty minutes. It was then chilled in liquid air and 15 mℓ of a (2:1) mixture of ether and dimethyl formamide* at -70° to -75°, were slowly added. The contents of the reaction vessel were warmed to -60° and after ten to fifteen minutes SF_4 was distilled under vacuum into the adjacent receiver. The SF_4 was hydrolysed with an ice-cold NaOH solution (16 per cent) and the residue in the reaction vessel was first hydrolysed with five to ten mℓ of ice-cold water and then made alkaline with NaOH solution. The two solutions were heated in a steam bath for a few minutes to evaporate most of the ether. After cooling they were diluted to 250 mℓ and the F^{18} activity was measured. The SF_4 fraction distilled did not give the colour reaction for silica with ammonium molybdate reagent128,132).

The above experiment was also repeated using SiF_4^{18} and SF_4 in the ratio 1:2.

Determination of the Specific Activity of SiF_4^{18}

About 500 mℓ of SiF_4^{18}, at atmospheric pressure, were condensed in the reaction vessel D (Fig.7) followed by addition of 15 mℓ of a (2:1) ether-dimethyl formamide mixture. On warming the reaction

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* NOTE: The melting point of DMF is -61° 149) but a (2:1) mixture of ether and dimethyl formamide remains liquid until -75°.

vessel a white crystalline precipitate of the complex $SiF_4.(DMF)_2$ was obtained. It was hydrolysed with 10 mℓ of ice-cold water and then made alkaline with NaOH solution. The reaction vessel was heated in a steam bath tovolatalize most of the ether. A clear solution was obtained when it was diluted to 250 mℓ. A 5 mℓ portion of this solution was used for counting F^{18}.

The solutions obtained in the preceding experiments were analysed for SiF_4 and SF_4. The activity of F^{18} transferred to SF_4 was calculated from the counting and analytical data. The results are given in Table 23.

Exchange of F^{18} between ${SiF_4}^{18}$ and SF_4 in gas phase

Another experiment was done to investigate the exchange of F^{18} between ${SiF_4}^{18}$ and SF_4 in the gas phase. The experimental arrangement was the same as in the preceding experiment. The bulb C (Fig.8) was filled with ${SiF_4}^{18}$ at 37-38 cm of mercury. Then SF_4 was introduced till the pressure of the gases in C became equal to atmospheric pressure. The mixture of ${SiF_4}^{18}$ and SF_4 was kept at room temperature for thirty minutes, but no visible reaction could be detected. About 10-15 mℓ of dimethyl formamide was added to the reaction vessel D (Fig.7). The reaction vessel was cooled to -30° in order to reduce the vapour pressure of DMF. Then the ${SiF_4}^{18}$ - SF_4 mixture was slowly bubbled through the DMF, which removed ${SiF_4}^{18}$ from the mixture as solid ${SiF_4}^{18}.(DMF)_2$. When no more ${SiF_4}^{18}$ -SF_4 could be bubbled through the DMF, the stop cock 1 (Fig.7) was closed and the reaction vessel was opened to the receiver E (Fig.7) in order to remove most of the volatile products. The remaining

TABLE 23

F^{18} Exchange between SF_4 and SiF_4^{18} at -60° to -65°

		(1:1) SiF_4^{18}-SF_4		(1:2)SiF_4^{18}-SF_4
		I	II	
1.	Counts min^{-1} g^{-1} for SiF_4^{18} at zero time	49600	29090	79950
2.	Weight in g. of SiF_4^{18} in SiF_4^{18} - SF_4	1.4455	2.2013	2.214
3.	Weight in g. of SF_4 in SiF_4^{18} - SF_4	1.5010	2.2858	4.5684
4.	Weight in g. of SF_4 separated	0.89038	1.5313	2.5028
5.	Counts min^{-1} for SF_4 separated from SiF_4^{18} - SF_4 at zero time	19585	20820	66360
6.	Counts min^{-1} for the residue	52500	43700	117500
7.	Counts min^{-1} for SiF_4^{18} at zero time (sum 5 and 6)	72085	64520	183860
8.	Counts min^{-1} for SiF_4^{18} at zero time (1 and 2)	71697	64036	177000
9.	Total counts min^{-1} transferred to SF_4 (3, 4 and 5)	36320	31120	121100
10.	Percentage of F^{18} transferred to SF_4 (7 and 9)	50.4	48.2	65.8

mixture was again bubbled through the DMF. When most of the mixture had thus been consumed the reaction vessel was warmed to room temperature and SF_4 was distilled into the receiver E for ten minutes. The distillate and the residue were hydrolysed and counted as usual. No activity could be detected in the solution of the SF_4 collected in the receiver E.

Discussion

The absence of F^{18} exchange between SiF_4^{18} and SF_4 at room temperature shows that the two compounds do not interact in the gas phase. This observation is in agreement with the findings of Muetterties et al.$^{17)}$, as far as the interaction at room temperature is concerned. The interaction between the two compounds through the lone pair of electrons on the sulphur atom, which would also result in the above observation, can be ruled out, because the two compounds exchanged fluorine when condensed together.

The high melting point of the SiF_4 and SF_4 mixtures in relation to the melting point of the constituents and the transfer of F^{18} to SF_4 at a low temperature show that SiF_4 and SF_4 interact. It is suggested that the exchange of F^{18} between SF_4 and SiF_4^{18} takes place via bridging fluorine atoms. The exchange via SiF_6^{2-} is not likely because SiF_4 is weaker F^- ion acceptor than BF_3 and the latter does not extract F^- from SF_4 (Chapter 5).

Vapour Pressure Measurements of SiF_4 - SF_4 systems.

If SiF_4 and SF_4 molecular complexes exist at low temperatures, a significant difference between the vapour pressure of the adduct and the vapour pressures of SiF_4 and SF_4 at the corresponding temperatures would be expected. The vapour pressures of the SiF_4 - SF_4 system was studied at several temperatures between -20° and -130° to obtain further information on the SiF_4 - SF_4 adduct.

For the determination of the vapour pressure a static method was employed. The experimental arrangement is shown in Fig.22. The container A was evacuated and dried under vacuum for a few hours. The container was then cooled in liquid air and the two gases, in the desired proportion, were condensed into it. The stop cock 1 (Fig.22) was closed and the container was placed in an n-pentane bath at -130°. The bath was slowly warmed to the desired temperature and maintained at this temperature for about ten minutes to attain thermal equilibrium. The the vapour pressure was determined from the heights of the mercury columns.

Discussion

A comparison of the Tables 24 and 25 show that the vapour pressures of the mixtures of SiF_4 and SF_4 are considerably less than the sum of the vapour pressures of the components at corresponding temperatures. For example, the vapour pressures of (1:1) SiF_4 - SF_4 and (1:2) SiF_4 - SF_4 at -90° are 34.3 cm and 14.7 cm respectively, while at the same temperature the sum of the vapour pressures of the components is 136.9 cm. This may be considered as an indication of compound formation between SF_4 and SiF_4.

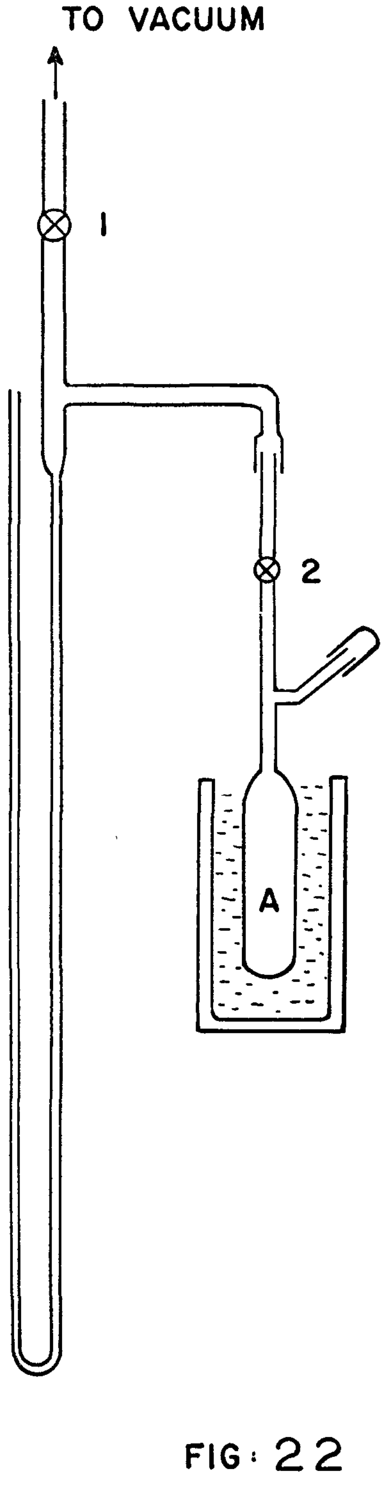


FIG: 22

TABLE 24

Vapour Pressure of SiF_4 - SF_4 Mixtures

Temperature	SiF_4 - SF_4 Mixtures per cent of SiF_4										
	10%	20%	25%	28.6%	33.3%	40%	50%	60%	66.7%	71.4%	75%
-125°	0.0	0.0	0.5	0.7	0.4	0.8	0.7	0.7	0.7	0.8	0.8
-120°	0.0	0.2	0.8	0.9	0.8	1.8	2.7	1.1	1.0	1.9	1.9
-110°	0.2	0.4	0.7	1.2	7.4	7.7	8.8	8.5	9.1	10.7	10.0
-100°	0.8	0.8	1.1	1.5	12.7	19.0	23.3	19.5	29.4	28.5	29.1
-90°	2.1	2.3	1.7	2.4	14.7	23.3	34.3	33.9	33.4	60.6	72.1
-80°	6.0	8.0	6.3	6.7	17.0	26.3	42.5	56.7	80.4	103.6	128.6
-70°	17.0	22.2	19.2	16.3	22.4	31.6	51.4	69.1	95.9	122.1	-
-60°	36.6	39.0	45.4	43.8	401.	50.7	58.8	76.3	103.1	131.9	-
-50°	49.6	50.5	72.9	73.2	62.2	69.5	68.6	94.0	110.8	144.0	-
-40°	63.0	62.7	100.2	96.5	94.4	91.3	88.3	91.6	129.0	-	-
-30°	88.8	86.1	120.2	115.0	106.6	106.4	98.4	-	-	-	-
-20°	132.2	126.7	-	142.9	132.5	131.2	123.5	-	-	-	-

TABLE 25

Vapour Pressure of SiF_4 and SF_4

Temperature	Vapour Pressure in cm of Mercury SF_4	SiF_4 This work	SiF_4 188) Reported	Temperature
-130°	-	0.8 cm	2.2 cm	-125.1°
-128°	-	-	-	-
-120°	0.3	5.5	4.2	-121.5°
-110°	0.7	17.2	16.2	-110.7°
-100°	1.9	49.8	51.5	-99.8°
-95°	-	75.2	77.8	-95.5°
-90°	4.1	132.8	131.7	-90.5°
-80°	7.9	-	207.7	-84.0°
-70°	15.6	-	242.8	-81.0°
-60°	27.0	-	323.8	-75.5°
-50°	45.6			
-45°	57.8			
-40°	76.8			
-35°	97.0			
-30°	122.6			

F^{19} NMR Spectroscopy of SiF_4 - SF_4 Systems

The preceding results indicate that SiF_4 and SF_4 combine at low temperatures probably to form molecular complexes. Therefore, the F^{19} NMR spectra of SiF_4 - SF_4 system was reinvestigated between room temperature and -100°.

An NMR sample was prepared containing 500 mℓ of SiF_4 at 20 mm of mercury and 500 mℓ of SF_4 at 80 mm of mercury. The pyrex glass NMR sample tube became foggy as soon as it was warmed to room temperature and after some time a white amorphous precipitate settled down. This observation was unexpected because dry glass does not react with SF_4 or SiF_4. However, the F^{19} NMR spectrum of the sample was recorded between -30° and -110°. Two F^{19} resonance signals were observed which were about 248 ppm apart at -30°, and 213 ppm apart at -110°. The fact that the mixuture remained liquid down to -110° was in contradiction to the previous observations that a solid was obtained until -55°. This phenomenon could be explained by assuming that under pressure either SF_4 or SiF_4 reacted with the glass and the two signals were due to SOF_2 and SiF_4. This was found to be the case, as explained later.

In order to arrive at a definite conclusion regarding the above assumption and interaction between SiF_4, and SF_4 it was necessary to compare the NMR spectra of SiF_4, SF_4 and SiF_4 - SF_4. Since quartz NMR tube of 1 mm wall thickness can be subjected to pressures up to 50 atmospheres and is more resistant towards reactive fluorides than pyrex, the samples were made in quartz NMR tubes. In preparing these samples maximum care was taken to eliminate traces of moisture. When the samples were warmed to room temperature the SF_4 and SiF_4 - SF_4 samples remained clear, but the tube containing SiF_4

turned a little foggy, indicating that a reaction had taken place. The F^{19} NMR spectra of these samples were recorded between -30° and 85°. A single sharp peak was obtained from the SiF_4 sample at all temperatures, the SF_4 signal was about 90 cps wide at room temperature and broadened further as the temperature was lowered, as reported by Muetterties et al.6). The SiF_4 - SF_4 sample gave two peaks at all temperatures between -30° and -85°, and the SF_4 peak was considerably broader than the SiF_4 peak. However, below -80° the SF_4 signal disappeared and only SiF_4 and SOF_2 could be observed down to -110°. In the freshly prepared sample of SiF_4 - SF_4 the meniscus of the liquid was distinct. After about two weeks it had disappeared, but reappeared on cooling the tube to -10° and the quantity of the liquid seemed to be more than originally present. After three weeks the spectrum of the sample of SF_4 remained unchanged, but the spectrum of the SiF_4 sample was broad at room temperature, at -30° it consisted of two partially overlapping peaks (Fig.25) which broadened and could no longer be distinguished as separate peaks at -60°. The change in the spectrum of SiF_4 - SF_4 was also pronounced. The SF_4 signal had become very broad and weak and the SF_4 and SOF_2 lines had grown in intensity (Fig.23).

Again fresh samples containing SiF_4 and SF_4 in the approximate proportion, (1:1), (1:2) and (2:1) respectively were prepared. The samples were stored in liquid air before taking the spectrum. The (1:1) and (1:2) mixtures of SiF_4 and SF_4 gave single peaks of both the components, i.e. the SF_4 signal was broad but the SiF_4 signal was sharp.

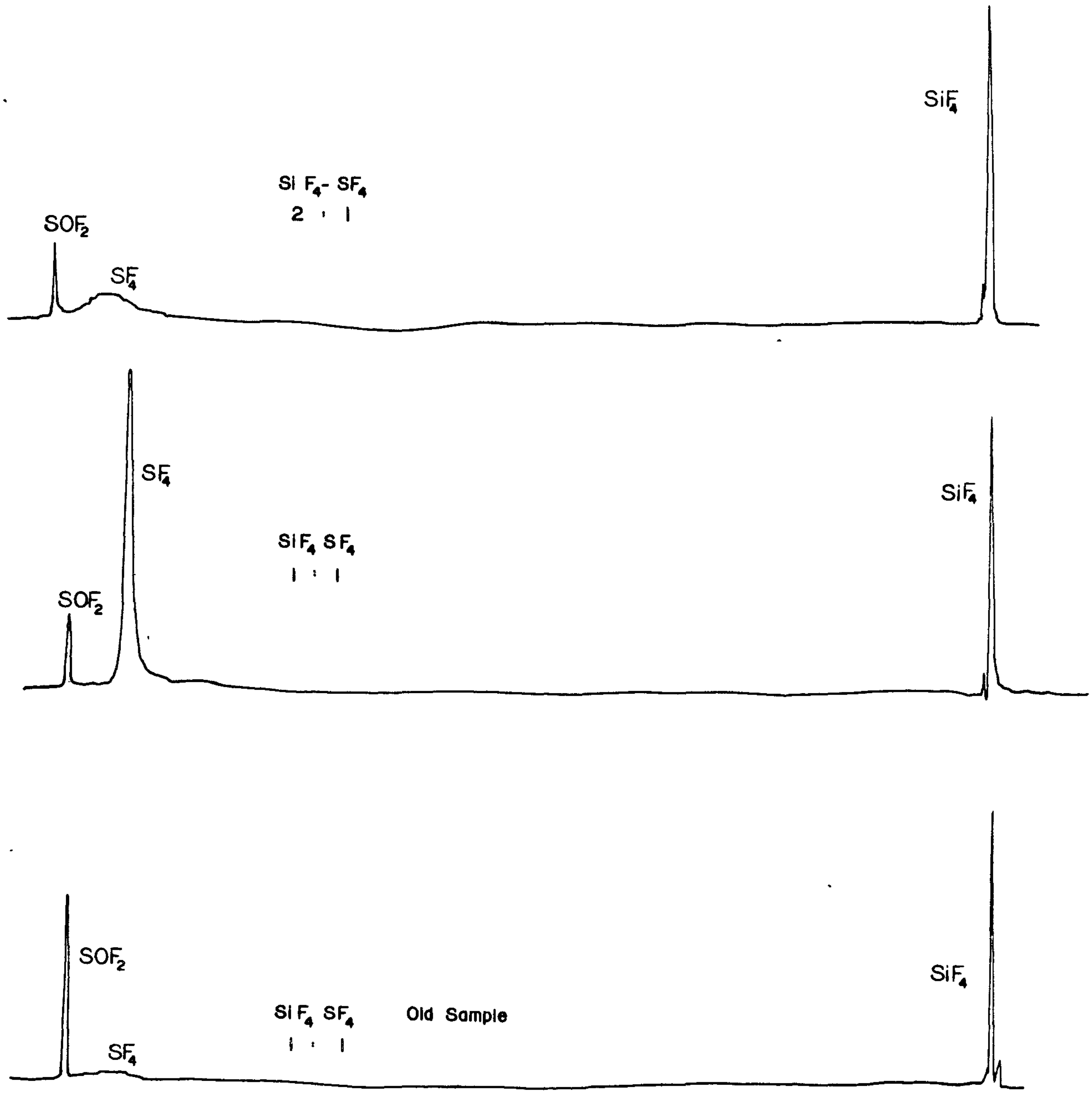


FIG 23 F^{19} NMR of SiF$_4$–SF$_4$ at room temperature

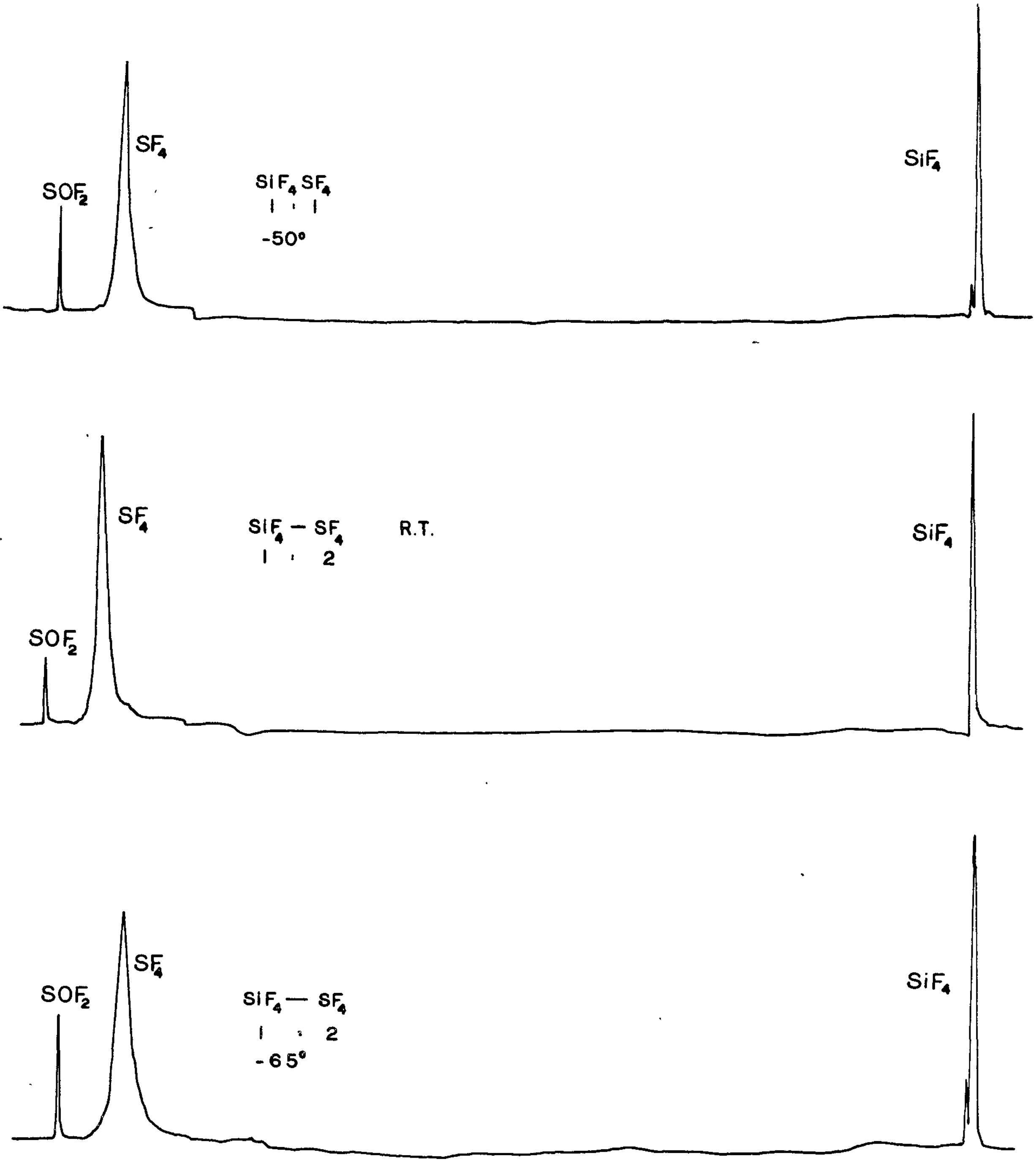
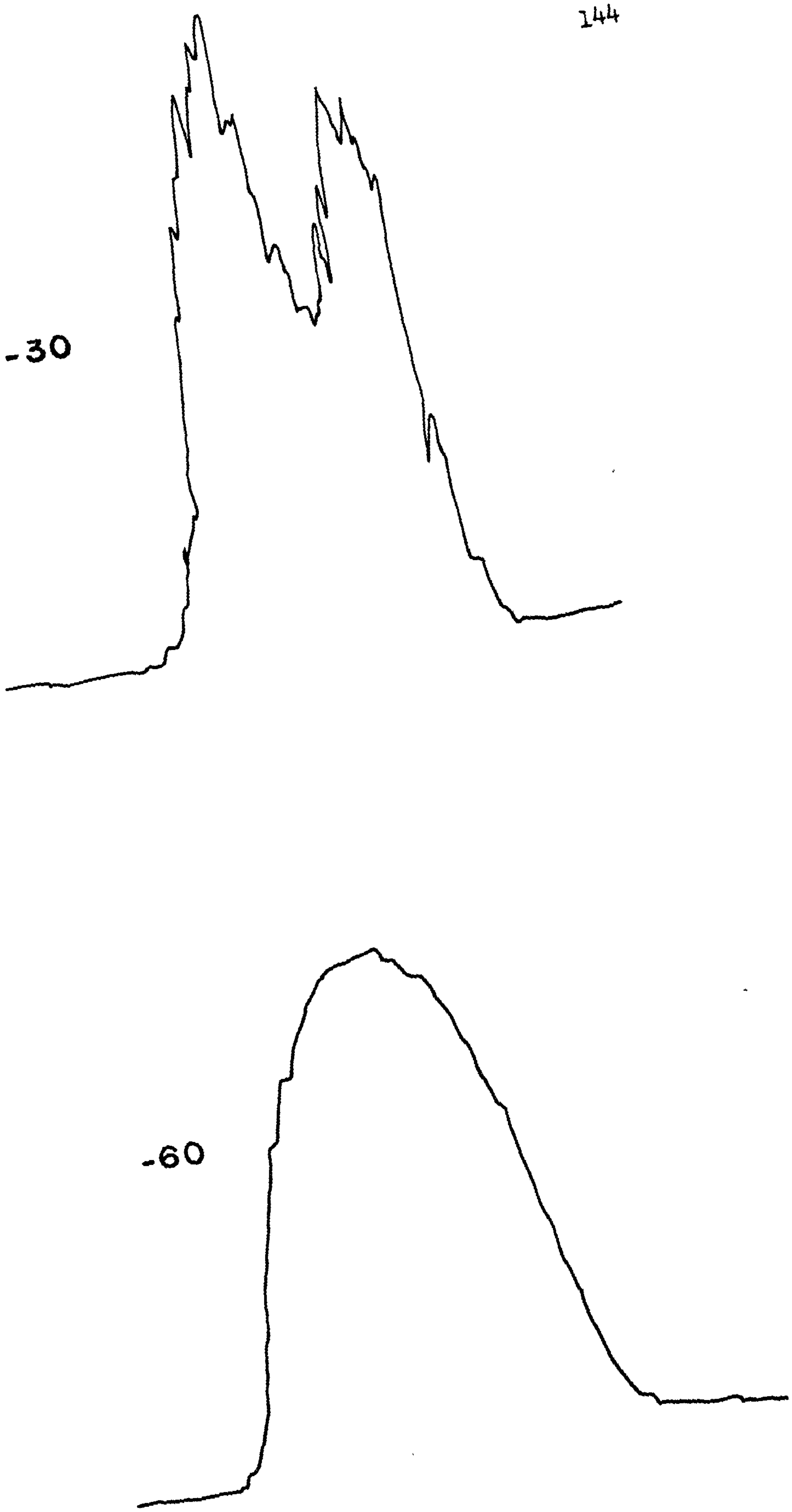


FIG24-F^{19} NMR-FRESH SAMPLES



F^{19} NMR of SiF_4

FIG· 25

As the temperature was lowered the SF_4 signal narrowed and finally below the freezing point of the mixture disappeared (Fig.24). The SF_4 peak in the (2:1) mixture was very broad like that in the three week old sample (Fig.23). The chemical shifts and the peaks widths of the SiF_4 and SF_4 signals are given in Tables 26 to 28.

Discussion

As reported by Muetterties et al.17) SiF_4 and SF_4 do not appear to interact with each other in the liquid phase. However, it was observed that as the temperature was lowered the two peaks drew closer together, which may be considered as an indication of weak interaction.(Table 26).

The F^{19} resonance signals of the (1:1) mixture of SiF_4 and SF_4 faded away at about -60° showing that a solid complex of SF_4 and SiF_4 had been formed. Similarly in the (1:2) mixture formation and the solid complex was observed at -85°. It is, therefore, suggested that the complexes of SiF_4 with SF_4 exist only in the solid state but they are completely dissociated in liquid phase.

It was observed that at room temperature SiF_4 - SF_4 sealed in a pyrex glass NMR tube reacted with the glass and all the SF_4 was decomposed, the quartz tube containing SiF_4 became foggy and in the (1:1) SiF_4 - SF_4 sample, sealed in a quartz tube, the quantity of SF_4 decreased with time; the F^{19} NMR spectrum of (1:1) SiF_4 - SF_4 became similar to the (2:1) SiF_4 - SF_4 spectrum (Fig.23). On the basis of these observations it is suggested that SiF_4 reacts slowly with

TABLE 26

SiF_4 Chemical Shifts in SiF_4 - SF_4 with respect to SF_4

Temperature	SiF_4 and SF_4 separate samples	SiF_4 - SF_4 Mixtures (1:1) SiF_4 - SF_4 50% SiF_4	(1:2) SiF_4 - SF_4 33.3% SiF_4	(2:1) SiF_4 - SF_4 66.7% SiF_4
Room tem.	236.2 ppm	225.3 ppm	222.8 ppm	229.7 ppm
-30°	--	224.6 ppm	221.5 ppm	228.8 ppm
-50°	--	222.7 ppm	--	--
-60°	--	--	--	225.1 ppm
-65°	--	--	219.1 ppm	--

TABLE 27

Widths of SF_4 Peaks at Half Maximum Height

		SiF_4 - SF_4 Mixtures			
Temperature	SF_4 alone	50% SiF_4	33.3% SiF_4	66.7% SiF_4	50% SiF_4 - SF_4 3 week old sample
Room Temperature	90.0 cps	105 cps	145.3 cps	-	-
-30°	-	79.1 cps	74.2 cps	595 cps	650 cps
-45°	1300	-	-	-	-
-50°	-	71.8cps	150.7cps	694 cps	-
-65°	-	-	188.0 cps	-	-

TABLE 28

Widths of SiF_4 peaks at Half Maximum Height in cps

Temperature	SiF_4 Alone		SiF_4 - SF_4 mixtures		
	Fresh sample	3 weeks' old sample	50% SiF_4	33.3% SiF_4	66.7% SiF_4
R.T.	-	-	4.3	2.3	-
-30°	4.2	20.2	4.5	2.2	5.5
-50°	3.5	-	3.9	4.3	-
-60°	-	46	-	-	4.0
-65°	-	-	-	5.9	-

glass or quartz under high pressure producing an oxyfluoride which in turn reacts with SF_4 yielding SOF_2 and SiF_4

$$SiF_4 + SiO_2 \longrightarrow (SiOF_2)_n$$

$$(SiOF_2)_n + SF_4 \longrightarrow SOF_2 + nSiF_4$$

The assumption that at room temperature and under high pressure SiF_4 reacts with quartz, is supported by the following observations. A fresh sample of SiF_4 which was not warmed above -30° gave one sharp F^{19} resonance signal at all temperatures between -30° and -90°. But the F^{19} resonance signal of the old SiF_4 sample at -30° was broad and showed two overlapping peaks (Fig.25) which merged together at -60°. The reaction between SiF_4 and quartz appears to be complex. However, it is suggested that the one of the two overlapping peaks may be due to one of the products of the reaction, $Si_2OF_6$150); b.p. -23.3° and m.p. -47.8°. Booth and Osten observed150) that after boiling off liquid SiF_4 from glass ampoules a small amount of a residue was left which voltalized at room temperature. The authors presumed it to be a volatile oxyfluoride produced by to partial hydrolysis of SiF_4. It is suggested that the oxylfluoride could have been produced as a result of the above mentioned reaction.

Infra-Red Absorption Spectrum of (1:1) SiF_4 - SF_4 and (1:2) SiF_4 - SF_4

The infra-red spectra of (1:1) SiF_4 - SF_4 and (1:2) SiF_4 - SF_4 at liquid air temperatures were examined and compared with the infra-red spectra of solid SF_4 (Chapter 5) and SiF_4. The procedure for preparing the I.R samples of solid SiF_4 - SF_4, SiF_4 - $2SF_4$ and SiF_4 was the same as described for $SF_4.BF_3$ (Chapter 5). The spectra were recorded between 250 and 2100 cm^{-1}. These spectra are shown in Fig.26 and the characteristic frequencies are given in Table 29 .

Discussion

The SiF_4 molecule is tetrahedral. It has four normal modes of vibration; ν_1 and ν_2 being symmetrical are infra-red inactive. The frequencies 1030 and 390 cm^{-1} have previously been assigned to ν_3 and ν_4 respectively151). The I.R. spectrum of gaseous SiF_4 (Table 29) contains six combination lines besides these two. The spectrum of solid SiF_4 consist of nine absorption peaks (Fig.26 ; Table 29). No prior spectroscopic observations of solid SiF_4 seem to have been reported. Therefore, an attempt has been made to assign the frequencies in the case of solid SiF_4 by comparing the spectra of SiF_4 in the two phases (Table 29).

In the crystalline state the site symmetry is often less than the molecular symmetry and as a consequence inactive modes become active. Thus in the case of solid SiF_4 the frequency ν_1 which is only active in the Raman in the gas phase appears in the I.R. spectrum of the solid at 830 cm^{-1} (Table 29).

By comparing the spectra of SiF_4 in the two phases, solid and gas, it may be concluded that solid SiF_4 contains simple tetrahedral molecules, and there is no evidence for association by fluorine bridging as has been shown by an X-ray crystal structure study of solid $SiF_4$66).

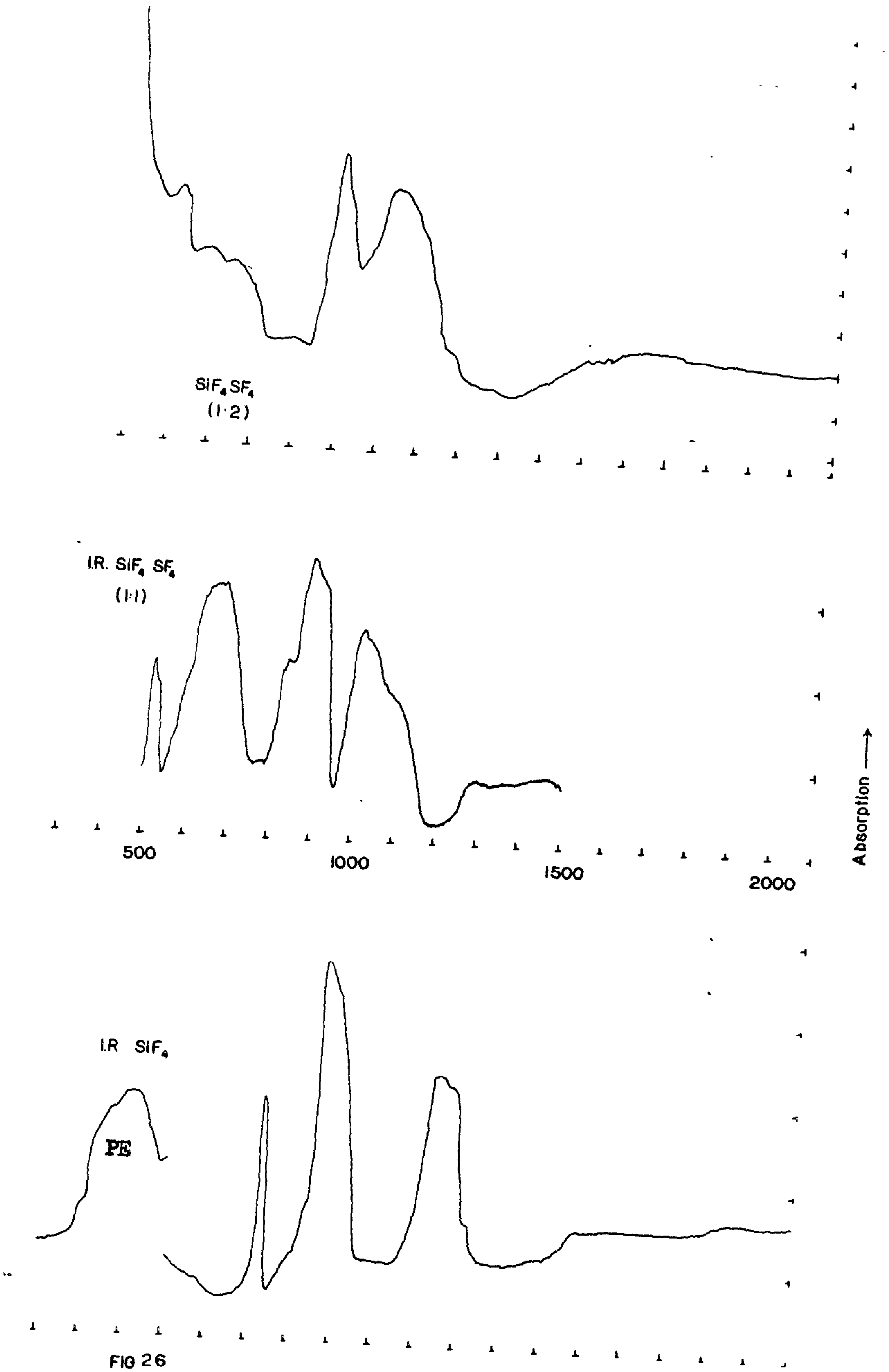

SiF$_4$ SF$_4$
(1:2)
I.R. SiF$_4$ SF$_4$
(1:1)
500
1000
1500
2000
Absorption ⟶
I.R SiF$_4$
PE

FIG 26

TABLE 29

I.R. Spectra of SF_4, SiF_4-SF_4 and SiF_4

Solid SF_4	(1:1) SiF_4-SF_4 solid Freq. cm^{-1}	(1:2) SiF_4-SF_4 solid Freq. cm^{-1}	Solid SiF_4 Freq. cm^{-1}	Solid SiF_4 Assignment	Gaseous SiF_4 137,151) Freq. cm^{-1}	Gaseous SiF_4 Assignment
	455 m				268 (Raman)	ν_2
520 S	515-530S	515-535 S	395 W	ν_4	391S	ν_4
			460S	$\nu_1 - \nu_4$		
			495-530S	$\nu_1 - \nu_2$		
		595 W	595 W	$\nu_3 - \nu_4$		
690S	675 m	650 W				
828 V.W	830-840 m	697 W	830 S	ν_1	780 m	$\nu_3 - \nu_2$
					800 (Raman)	ν_1
880 V.S 890 V.S 930 m	920S					
1018 W 1040 W 1150 m	1020S	1030S	970 V.S	ν_3	1010 1031 V.S.	ν_3
					1065 W	$\nu_2 + 2\nu_4$
					1161 W	$3\nu_4$
1290 S	1290 V.W		1248) 1285) S	$\nu_2 + \nu_3$	1191 m	$\nu_1 + \nu_4$
1723 V.S			1325 V.W	$4\nu_2 + \nu_4$	1827 m	$\nu_1 + \nu_3$
					2057 m	$\nu_2 + \nu_3$

A comparison of the spectrum of (1:1)SiF_4-SF_4 with that of solid SF_4 (Table29) shows that the SF_4 frequencies at 930, 940, 1145 and 1723 cm^{-1} are absent in the spectrum of the former. Also a comparison of the spectrum of solid SiF_4 with that of (1:1) $SiF_4.SF_4$ shows that the 395, 830, 970 and 1248cm^{-1} absorption bands of SiF_4 do not appear in the spectrum of (1:1) SiF_4 SF_4. The absence of the frequencies 1145 and 1723 cm^{-1}, and 978 and 1248 cm^{-1} from the spectrum of (1:1) SiF_4-SF_4 is significant because they are prominant in the spectra of the two components and thus may be taken as an indication of interaction between SF_4 and SiF_4. Moreover the comparable frequencies in the spectra of (1:1) SiF_4-SF_4 and the two solid components differ greatly in intensity, e.g. the absorption band at 1290 cm^{-1} is very strong in the spectrum of SF_4, strong in the case of SiF_4, but very weak in the case of (1:1) SiF_4-SF_4. The absence of the prominent I.R frequencies of solid SiF_4 and SF_4 from the I.R. spectrum of (1:2) SiF_4 - SF_4 indicates that the two fluorides form an adduct. Moreover the I.R. spectrum of (1:1) SiF_4 - SF_4 is markedly different from that of (1:2) SiF_4 - SF_4 (Table 29 , Fig.26) indicating that the two spectra belong to different compounds.

A common feature of the spectra of (1:1) SiF_4 - SF_4 and (1:2) SiF_4 - SF_4 is the presence of two bands of comparable frequencies and intensities at 900 ± 5 and 1025 ± 5 cm^{-1} (Fig.26, Table 29). The band at 900 ± 5 cm^{-1} has previously been assigned to SF_3^+ (Chapter 5). The band at 1025 ± 5 cm^{-1} can be assigned to the Si-F stretch by comparison with the I.R. spectrum of SiF_4 (Table 29).

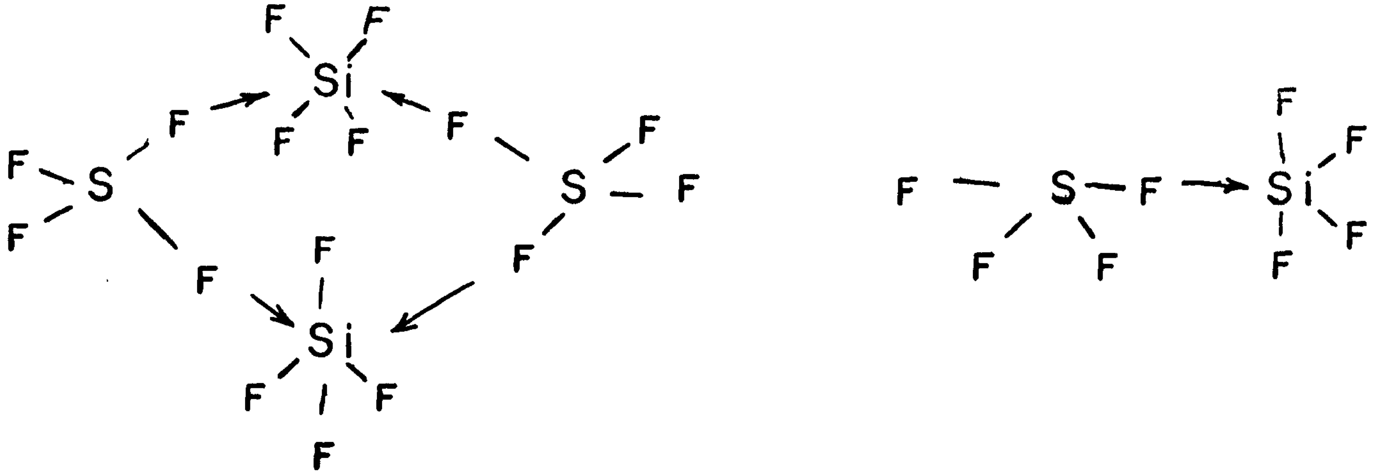
From the above discussion it is evident the SiF_4 and SF_4 form two adducts, viz: $SiF_4.SF_4$ and $SiF_4.(SF_4)_2$, in agreement with the previous conclusions.

By analogy with $SF_4.BF_3$ the silicon compounds would be expected to have a fluorine bridged structure. Possible structures of the two compounds are shown in Fig.27.

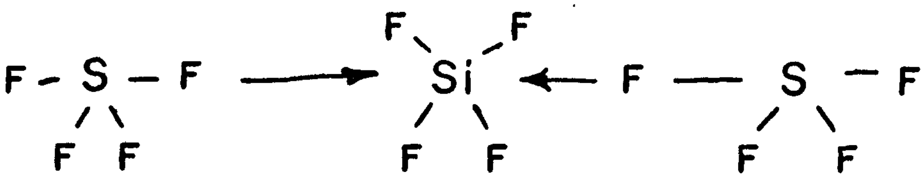
Conclusion

The evidence obtained from the F^{18} exchange study, vapour pressure measurements and I.R. spectroscopy of the SiF_4 - SF_4 systems shows that SiF_4 and SF_4 interact and probably form the two adducts $SiF_4.SF_4$ and $SiF_4.(SF_4)_2$. The information gathered from the F^{19} NMR spectra of SiF_4 - SF_4 systems indicate that in the liquid phase interaction between the two components is very weak, although the adducts $SiF_4.SF_4$ and $SiF_4.(SF_4)_2$ appear to be stable in the solid state.

Our experiment also indicates that under high pressure (about 50 atm) SiF_4 reacts with quartz at room temperature. This reaction has not been reported previously.



$SF_4 \cdot SiF_4$



$(SF_4)_2 \cdot SiF_4$

FIG. 27

CHAPTER 7

Exchange Reactions of POF_3 and SeF_4

POF_3 - BF_3 System

Compounds containing an oxygen atom generally form coordination complexes with the trihalides of boron[8,34]. Thus the formation of the adducts $POC\ell_3.BC\ell_3$, $POC\ell_3.BF_3$, $POF_3.BF_3$ and $POF_3.BC\ell_3$ is likely. The preparation of the first three compounds[36,152-155] has been claimed.

Burg and Ross[152] were the first to prepare the compound. $POC\ell_3.BC\ell_3$. They suggested that in this adduct oxygen is the donor They also attempted the preparation of $POC\ell_3.BF_3$ by passing BF_3 into a solution of $POC\ell_3$ in petroleum ether at -80° without success. However, Waddington and Klanberg[153] obtained a white solid by passing BF_3 into a solution of $POC\ell_3$ in liquid $HC\ell$, which melted at -3° with decomposition. It seems likely that $POC\ell_3$ behaves differently in petroleum ether than in liquid $HC\ell$. In 1961 Wiberg, et al.[154] reported the preparation of $POC\ell_3.BF_3$ under pressure in the range 0° to -30°. The possibility of forming a solid solution of BF_3 in $POC\ell_3$ cannot be ruled out because the melting point of the latter is 2°. Waddington and Klanberg[156] have reported that the P-O stretching frequency of $POC\ell_3.BF_3$ was almost the same as that of uncoordinated $POC\ell_3$, whereas the P-O stretching frequency of $POC\ell_3.SnC\ell_4$ was lowered by as much as 75 cm^{-1}. In view of the preceding discussion it seems unlikely that any of these authors prepared the adduct $C\ell_3PO \rightarrow BF_3$.

Booth and Walkup[36) established the existence of the adduct $POF_3.BF_3$ by the method of thermal analysis. They did not isolate the compound, however, by extrapolating the freezing-point curve they found the melting point of the adduct to be -20°. No other investigation of this compound has been published. The formation of this compound has been questioned by Topchiev et al.[34).

Recent conductometric and cryoscopic measurements have indicated that POF_3 is not protonated in 100 per cent sulphuric[157). This observation suggests that in $POF_3.BF_3$ bonding through the oxygen atom is not likely.

In 1960 Herber[158) studied the system $POC\ell_3$ - $BC\ell_3$ employing $C\ell^{36}$ as tracer and suggested that in $POC\ell_3.BC\ell_3$ oxygen is the donor. He postulated that the $C\ell^{36}$ exchange took place via an intermediate $[C\ell_4BO = PC\ell_3]^-$. The existence of such an intermediate is questionable since the boron atom cannot be pentavalent.

In 1961 Gerrard, et al.[159) obtained evidence for $BC\ell_4^-$ from the infra-red spectrum of the solid complex $POC\ell_3.BC\ell_3$.

In 1962 Wartenburg[160) reinvestigated the structure of $POC\ell_3.BC\ell_3$, at liquid air temperature employing infra-red and Raman spectroscopy. He concluded that the evidence favoured the formulation $C\ell_3\ PO\rightarrow BC\ell_3$. However, recent conductometric and cryoscopic measurements of $POC\ell_3$ solution in 100 per cent sulphuric acid indicate that $POC\ell_3$ is not protonated[157). This evidence shows that the oxygen atom in $POC\ell_3$ does not act as a donor towards the proton and therefore does not favour the Lewis acid-base type formulation of $POC\ell_3.BC\ell_3$.

In 1960 Gerding et al.$^{161)}$ measured the Raman spectrum of the liquid complexes $POC\ell_3.A\ell C\ell_3$ and $POC\ell_3.GaC\ell_3$. According to their interpretation of the spectra the two component molecules are bound through the oxygen atom of the $POC\ell_3$ molecule and no transfer of a $C\ell^-$ occurs as found for $NOC\ell.A\ell C\ell_3$$^{161)}$. Also the X-ray diffraction study of the $POC\ell_3$ complexes with the halides of Sb, Nb, Sn and Ti etc.$^{154,162-165)}$ has shown unequivocally that the bonding between $POC\ell_3$ and the metallic chloride is through oxygen of the $POC\ell_3$ molecule.

In 1963 Lewis and Sowerby$^{166)}$ studied $C\ell^{36}$ exchange between $POC\ell_3$ and the group III metallic chlorides. On the basis of their observations they have suggested that the complexes may be formulated as involving a bond between a chlorine atom and the metal; $OPC\ell_2$-$C\ell$ - - - - $MC\ell_3$, i.e. chlorine bridge. This may also be applicable in the case of the adduct $POC\ell_3.BC\ell_3$.

Thus various investigations of the $POC\ell_3$ - metal halide complexes showed different and conflicting results, either oxygen$^{156,161-165,167,168)}$ or chlorine atoms have been proposed as donors$^{154,166,169,170)}$, i.e. the compounds have been formulated as (I) $C\ell_3PO \rightarrow MC\ell_x$ or as (II) $POC\ell_2^+ \; MC\ell^-_{(x+1)}$. The existence of $POC\ell_2^+$ has not been unequivocally demonstrated$^{158,166)}$, however, Lewis and Sowerby$^{171)}$ have concluded from their $C\ell^{36}$ exchange studies that $POC\ell_4^-$ is formed, i.e. $POC\ell_3$ is a Lewis acid.

In all the formulations suggested for $POC\ell_3.BC\ell_3$ no worker has considered that $POC\ell_3$ could be a $C\ell^-$ ion acceptor$^{171)}$. The structure of $POC\ell_3.BC\ell_3$ is still in a confused state.

In view of the conflicting evidence on the structure of $POC\ell_3.BC\ell_3$ and the lack of knowledge concerning $POF_3.BF_3$ and $POC\ell_3.BF_3$

it was decided to study the F^{18} exchange between POF_3 and BF_3.

Exchange of F^{18} between BF_3^{18} and POF_3, on the formation of the adduct $POF_3.BF_3^{18}$

The experimental arrangement used was identical with that described for $SF_4.BF_3$ (Figs.7 and 8). About 550 mℓ of purified POF_3 at atmospheric pressure werecondensed in the reaction vessel at about -185°. An equal volume of BF_3^{18} was condensed on the POF_3 in three equal portions. Each time after condensing the BF_3^{18} the reaction vessel was slowly warmed to about -39°. The reaction vessel was warmed to -39° because at this temperature both the components are gaseous and in case the complex $POF_3.BF_3$ is not formed the combined pressure of the components would not damage the apparatus. At all temperatures up to -39°, during the addition of BF_3^{18}, only a solid phase could be observed. When all the BF_3^{18} had been added the reaction vessel was warmed to -30° and a white crystallic compound, similar to $SF_4.BF_3$ in appearance was obtained. The compound was cooled to -100° to -110° and pumped for a short time to remove any unreacted BF_3^{18}. Then the complex $POF_3.BF_3$ was chilled in liquid air and about 10 mℓ of ether, cooled to dry-ice temperature, were added to the adduct and the reactants were warmed. When the temperature reached -50° a vigorous reaction took place. After the reaction had subsided the contents of the reaction vessel were warmed to -30° and POF_3 was collected in the receiver for about five minutes. Then the contents of the two vessels were hydrolysed with ice-cold NaOH solution (16 per cent). Each solution was diluted to 250 mℓ and then counted for F^{18}. The POF_3 fraction distilled over, had considerable activity. The POF_3 solution did not give the colour reaction with turmeric characteristic of boron132). Thus showing that the activity in POF_3 was not due to contamination with BF_3^{18}. The solutions were analysed for BF_3 and POF_3. From the counting and analytical data the percentage of F^{18} transferred to POF_3 was calculated. The results of this study are given in Table 30.

Discussion

The visual observation confirmed the existence of the adduct $POF_3.BF_3$ It was found that about 33 per cent of the fluorine-18 activity is transferred to POF_3 on decomposing the complex $POF_3.BF_3^{18}$ at -30°.

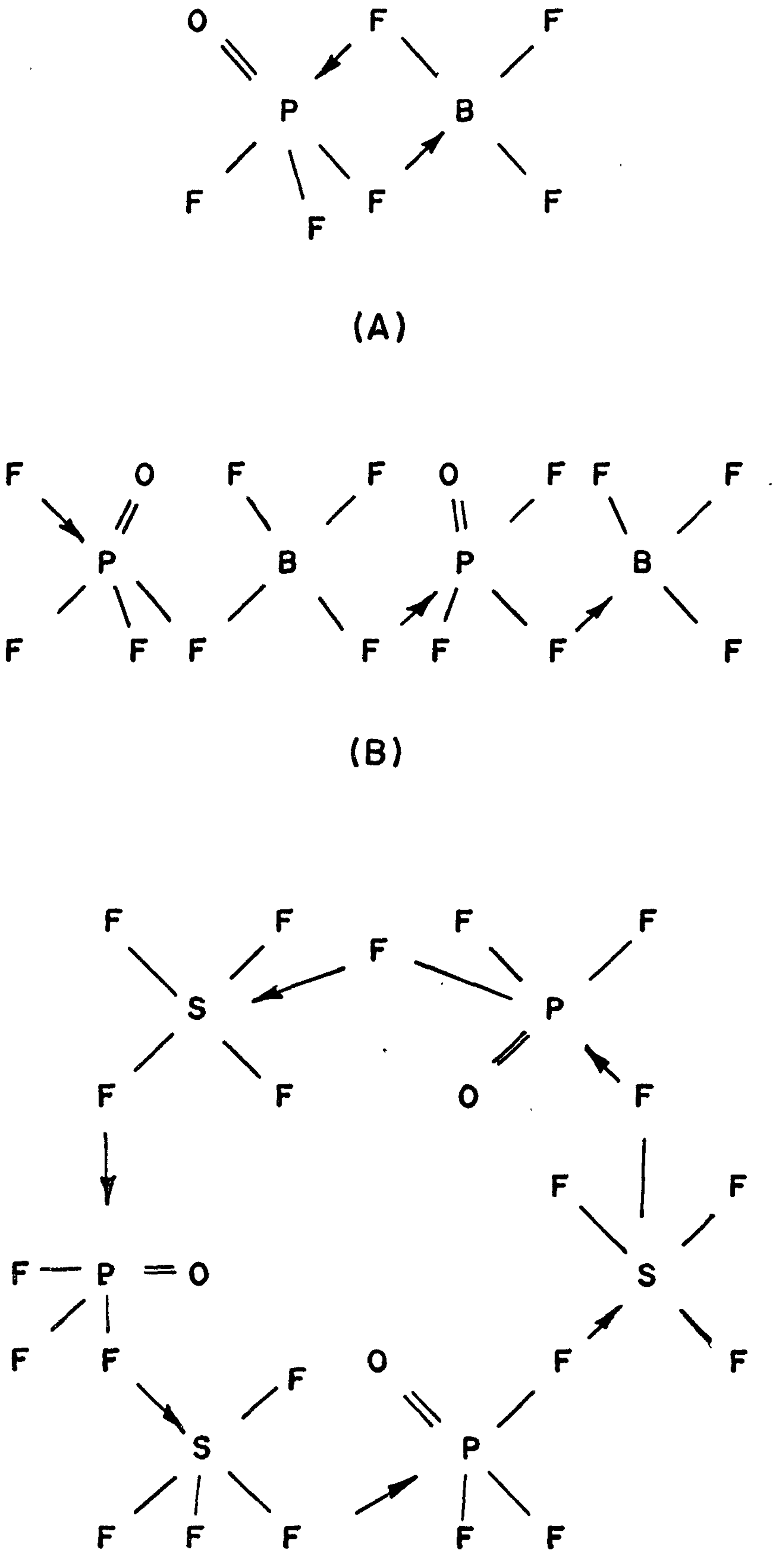
If in the adduct $POF_3.BF_3^{18}$ fluorine atoms exchange completely between the compounds 50 per cent of the F^{18} activity would be transferred to POF_3. The same amount of the activity would be transferred to BF_3, if POF_3^{18} were used for making the adduct. This result would be expected if the structure of the solid complex is either ionic $POF_2^+\ BF_4^-$ or covalent involving fluorine bridge (Fig.28). Assuming that the solid adduct $POF_3.BF_3$ is in rapid equilibrium with its vapours, the exchange of F^{18} would be accounted for by the following dissociative mechanisms:

$$\text{(Ionic)}\quad \underset{(S)}{POF_2^+} + \underset{(s)}{BF_4^-} \rightleftharpoons \underset{(G)}{POF_3} + \underset{(G)}{BF_3} \qquad (1)$$

TABLE 30

Exchange of F^{18} between BF_3^{18} and POF_3 in $POF.BF_3^{18}$ at -30°

1.	Counts min^{-1} $g.^{-1}$ for BF_3^{18} at zero time	33230
2.	Weight in g. of BF_3^{18} in the complex $POF_3.BF_3^{18}$	1.357
3.	Weight in g. of POF_3 in the complex $POF_3.BF_3^{18}$	2.0817
4.	Weight in g. of POF_3 separated from $POF_3.BF_3^{18}$	1.1689
5.	Counts min^{-1} for POF_3 separated from $POF_3.BF_3^{18}$ at zero time	8860
6.	Counts min^{-1} for the residue at zero time	36000
7.	Counts min^{-1} for BF_3^{18} in the $POF_3.BF_3^{18}$ (sum of 5 and 6)	44860
8.	Counts min^{-1} for BF_3^{18} in the complex at zero time (1 and 2).	45 093
9.	Total counts min^{-1} transferred to POF_3 at zero time (3, 4 and 5)	15778
10.	Percentage activity transferred to POF_3 (7 and 9)	35.2


O F F
P B
F F F F
F O F F O F F F
P B P B
F F F F F F F F
F F F F
F
S P
F F O F
F F
F — P = O S
F F O F F
S P
F F F F F

(A)

(B)

(C)

FIG 28

(Fluorine Bridge) $$\underset{(S)}{POF_3BF_3} \rightleftharpoons \underset{(G)}{POF_3} + \underset{(G)}{BF_3} \qquad (2)$$

Note: S = solid

G = gas

The result of the exchange allows one to reject the Lewis acid - Lewis base type structure of $POF_3.BF_3$ involving a coordinate bond from oxygen to boron, which would not lead to any exchange. It is, therefore, evident that the complex has either an ionic or a fluorine bridge covalent structure (Fig.28).

If it is assumed that on the formation of the compound $POF_3.BF_3^{18}$ at sufficiently low temperature the exchange of F^{18} due to the dissociative mechanisms is negligible and no other exchange mechanism is operative, and the complex has an ionic structure then on decomposing it by a metathetical reaction 25 per cent of the activity would be transferred to POF_3. Under the same conditions, if it is assumed that the adduct has a fluorine bridged structure then on decomposing the complex 16.7 per cent of the activity would be transferred to POF_3 provided that the strength of the bridge bonds P-F and B-F is comparable. The same results would be obtained if POF_3^{18} were used for making the complex.

On the basis of a single exchange experiment it is not possible to distinguish between the ionic or covalent formulation of $POF_3.BF_3$. Nevertheless the following points are worth considering. There is no conclusive evidence that POF_2^+ 166) is formed. The P-F bond in POF_3 is considerably shorter than any of the S-F bonds in SF_4 (Chapter 2), in other words the fluorine is more firmly attached to the phosphorus atom in POF_3 than to the sulphur atom in SF_4. By analogy with the structure proposed for $SF_4.BF_3$ (Chapter 5), it is suggested that the adduct $POF_3.BF_3$ has a structure involving briding fluorine atoms (Fig.28) similar to that of $SF_4.BF_3$. A fluorine bridge structure of $POF_3.BF_3$ implies that POF_3 would also function as a F^- acceptor like SF_4 in $SF_4.BF_3$ (Chapter 5). Some evidence that POF_3 is a F^- acceptor is given by the following experiment.

Exchange of F^{18} between POF_3 and LiF^{18}

The solid gas phase exchange reaction between LiF^{18} and POF_3 was studied in order to provide some evidence for the Lewis-acid property of POF_3. The same procedure was followed as for labelling SF_4, AsF_5 and PF_5. The temperature of the reaction tube was kept between 150° - 200°. The labelled POF_3 was purified from any possible contamination with HF^{18} by condensing it over anhydrous KF followed by evaporation at -39°. The count rate of POF_3^{18} was determined by the usual procedure and was found to be of the order of 4.5×10^4 cpm/g. of POF_3.

Lewis and Sowerby[171)] have suggested that the $C\ell^{36}$ exchange in the system $MC\ell^{36}$ - $POC\ell_3$ takes place via $POC\ell_4^-$, it is, therefore, suggested that in the system LiF^{18} - POF_3 the exchange would involve the POF_4^- ion.

$$LiF^{18} + POF_3 \longrightarrow LiPOF_4^{18} \longrightarrow LiF + POF_3^{18}$$

The intermediate $LiPOF_4$ would be expected to be unstable because of the small size and high polarizing power of Li^+ and relatively weak acceptor strength of POF_3, probably comparable with SF_4.

Ruff and Lustig[63)] have reported that SOF_4 forms a complex with CsF which has the ionic structure, $Cs^+ SOF_5^-$. The sulphur atom in SOF_4 is surrounded by five atoms while the phosphorus atom in POF_3 has four atoms around it. Thus the sulphur atom in SOF_4 is more sterically hindered than the phosphorus atom in POF_3, and the former would be expected to be a weaker acceptor of F^- than the latter. One might conclude, therefore, that POF_3 would be a stronger F^- acceptor than SOF_4.

As a corollary of the foregoing experiments and discussions it is suggested that POF_3 would form 1:1 adducts with PF_5, AsF_5 and SbF_5, and these adducts would be at least as stable as $POF_3.BF_3$. It is also suggested that ionic fluorides having large cations would form stable ionic complexes with POF_3, e.g. $CsPOF_4$ and $(CH_3)_4NPOF_4$. Also, there is a strong possibility that simple coordination compounds would be formed between POF_3 and organic bases such as trimethylamine, pyridine, ether and tetrahydrofuran, etc. (c.f. SF_4 coordination compounds, Chapter 8).

$SeF_4.BF_3$

Bartlett and Robinson[23,24,25)] prepared $SeF_4.BF_3$ by distilling SeF_4 and a large excess of BF_3 into a trap at about -185° and then warming the reactants to room temperature under dry air.

Excess BF_3 was evolved and a white solid melting at 50° remained. Due to the large difference in the melting point of SeF_4 and the boiling point of BF_3 this method did not ensure complete reaction between the components. Therefore, Whitla[136)] prepared this compound by bubbling BF_3 through SeF_4 and then removing the unreacted SeF_4 by vacuum distillation. The melting point of the complex was found to be 45°.

Although Bartlett and Robinson suggested the ionic formulation, $SeF_4^+ BF_3^-$ for the complex $SeF_4.BF_3$ [23,24,25)] subsequent investigations[136)] employing infra-red, Raman and F^{19} NMR spectroscopy, and cryoscopy in nitrobenzene have shown that SeF_4 and BF_3 are probably bonded together by covalent fluorine bridges.

It was hoped to obtain further information on the structure of $SeF_4.BF_3$ by F^{18} tracer study similar to that already described for $SF_4.BF_3$.

Exchange of F^{18} between BF_3^{18} and SeF_4 on the formation of the adduct $SeF_4.BF_3^{18}$

None of the above procedures seemed to be practical for making $SeF_4.BF_3^{18}$ because a large amount of BF_3^{18} was required which was difficult to handle, therefore, an attempt was made to prepare $SeF_4.BF_3$ by gas phase reaction. The experimental arrangement and the apparatus employed in this investigation were similar to that described for $SF_4.BF_3$. The tube containing SeF_4 was joined to the reaction vessel in place of the 'cold funnel' (Fig.7) and the apparatus was evacuated and vacuum dried. Some SeF_4 was vapourized into E followed by a little BF_3^{18}, then E was cooled to 0° and excess BF_3^{18} was pumped off. The reaction vessel was again warmed to room temperature and the foregoing operation was repeated several times until enough $SeF_4.BF_3^{18}$ had been formed. A large excess of anhydrous $(CH_3)_3N$ was condensed on $SeF_4.BF_3^{18}$, cooled to about -180°. Then the reaction vessel was warmed to ambient temperature and the displaced SeF_4 was collected into the receiver E (Fig.7). In order to accelerate the rate of distillation of SeF_4 the reaction vessel was warmed to 40°. The contents of 'E' were decomposed and a dark red precipitate was deposited. The distillation of SeF_4 was stopped as soon as the reactants started changing colour. The distillate and the residue were hydrolysed with ice-cold NaOH solution and counted for F^{18} activity.

Discussion

The activity of the SeF_4 fraction distilled was of the order of 1000 cpm. The SeF_4 solution did not give the colour reaction with turmeric characteristic of boron132). Thus showing that the activity in SeF_4 was not due to contamination with BF_3^{18}. As in the case of $SF_4.BF_3$, the transfer of F^{18} to SeF_4 rules out the donor acceptor structure of $SeF_4.BF_3$.

This investigation was not pursued further because of experimental difficulties and limited time.

CHAPTER 8

Acceptor Properties of SF_4 and SeF_4

SF_4 - THF System: Fluorine Nuclear Magnetic Resonance

In the tracer study of the structure of $SF_4.BF_3$ the labelled compound was decomposed at various temperatures with tetrahydrofuran (THF) or ether. It was observed that when the compound is decomposed at -80° with excess THF, the SF_4 set free could not be distilled under vacuum although the melting point of THF is -108° [131] and that of SF_4 is -121° (Table 1). The reason for the above observation could be that SF_4, a weak acceptor [21,22] and tetrahydrofuran a fair donor [172,173] form a molecular complex which has a very low vapour pressure at -80°. Therefore, the fluorine nuclear magnetic resonance spectrum of the SF_4-THF system was studied between room temperature and -80°.

SF_4 - THF: Sample Preparation

The apparatus shown in Fig.29 was connected to the vacuum line, evacuated and vacuum dried. The NMR tube and the bulb A were then cooled in liquid air. About 500 $m\ell$ of purified SF_4 at 50 mm of mercury was condensed into A. The tube B was filled with about 10 $m\ell$ of anhydrous THF and was evacuated and THF was distilled into A under vacuum at -60°. When enough THF had been collected in A the stop

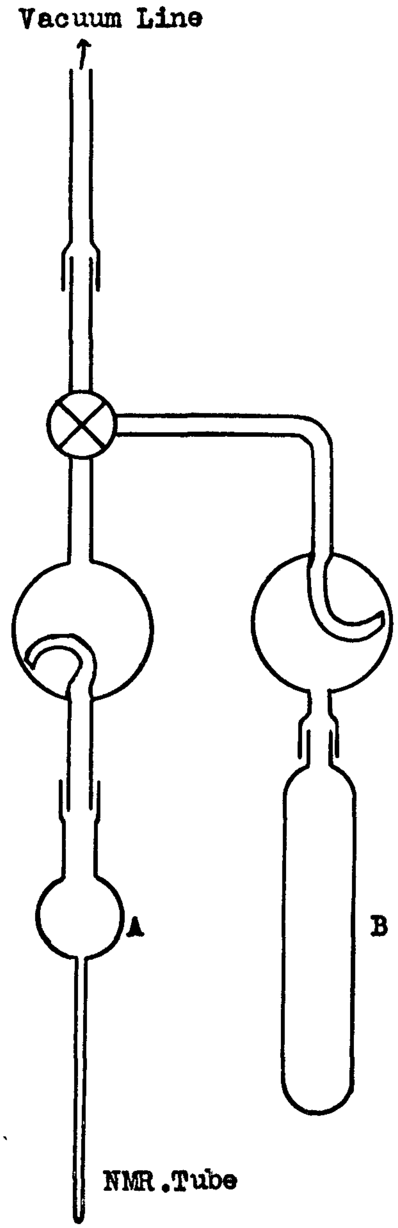


FIG.29

cock was closed and A was warmed to allow SF_4 and THF to run down into the NMR tube. The NMR tube was then cooled in liquid air and sealed. The concentration of SF_4 in the samples prepared as described was between 20 and 30 per cent.

Before taking the fluorine NMR spectrum of the sample it was kept at room temperature to observe its behaviour with time. The sample developed a greenish yellow colour at room temperature after four hours and became viscous. After another two hours it became thick like jelly. During the following two days the colour of the sample changed to greenish yellow, dark green and finally black. After two days the sample again became mobile, but there was a lot of sediment in the sample tube. This sample exploded after about six months. Another sample of SF_4 - THF was kept at -15°, it remained clear and mobile for over thirty-six hours, but after a week it showed slight change in appearance.

F^{19} NMR Spectrum of SF_4 - THF

As a result of the above observations the F^{19} resonance spectrum of the freshly prepared sample was taken between room temperature and -80°. In the fluorine resonance spectrum of SF_4 - THF at room temperature two very broad peaks were observed. As the temperature was lowered the peaks narrowed, at -25° to -30° they became sharp and showed a triplet structure. At -67° the appearance of the spectrum remained unchanged and when the temperature was lowered to -70° the fluorine signal vanished showing that the system had solidified. The chemical shifts and coupling constants of the triplets are given in Table 31. The NMR spectra of SF_4 - THF at different temperatures are shown in Fig.30.

Discussion

In 1958 Cotton, et al. 5) reported that the F^{19} NMR spectrum of SF_4 at -100° consisted of two triplets which were 48 ppm apart and which gave a coupling constant of 78 cps.

In 1959 Muetterties et al. 6) reported that at 23°, SF_4 displayed a single F^{19} resonance signal whose width at half height was about 90 cps. The width of the signal increased with lowering of the temperature. At -47° the signal split up into two resonances of equal intensity that became resolved at -85°. These authors found that at -98° the chemical shift between these triplets was 52 ppm and the coupling constant was 78 cps. Later work by Quail174) showed that the SF_4 signal splits into two triplets at about -60° if SF_4 is dissolved in an inert solvent such as CCl_4. It was also found that the effect of temperature on the separation of SF_4 triplets is not very great. The chemical shifts of the two triplets at -59° and -103° were found to be 53.2 ppm and 52.0 ppm respectively and the coupling constant was found to be 76.4 cps.

Muetterties et al.21) have reported the preparation of adducts between SF_4 and tertiary animes, e.g. pyridine trimethyl amine and N-methyl morpholine etc. They found that the adducts give a single sharp fluorine resonance peak. Therefore, they concluded that

TABLE 31

Chemical Shifts and Coupling Constants of SF_4, $SF_4.Et_2O$ and $SF_4.THF$ triplets

Temperature	Chemical Shifts between the two F^{19} resonances in ppm			Coupling Constant $J_{FF'}$ in cps		
	SF_4[177]	SF_4. THF	SF_4.Et_2O	SF_4	SF_4. THF	SF_4.Et_2O
-25°	-	-	52.4			
-28°	53.9	-	-			
-35°	-	47.4	-	78[5,6]		
-40°	-	47.1	52.1		66.4	74.3
-44°	53.6	-	-			
-50°	-	-	51.8	76.4[174]		
-67°	-	45.3	-			
-100°	-	-	50.9			
-103°	51.9	-	-			
-132°	-	-	48.1			

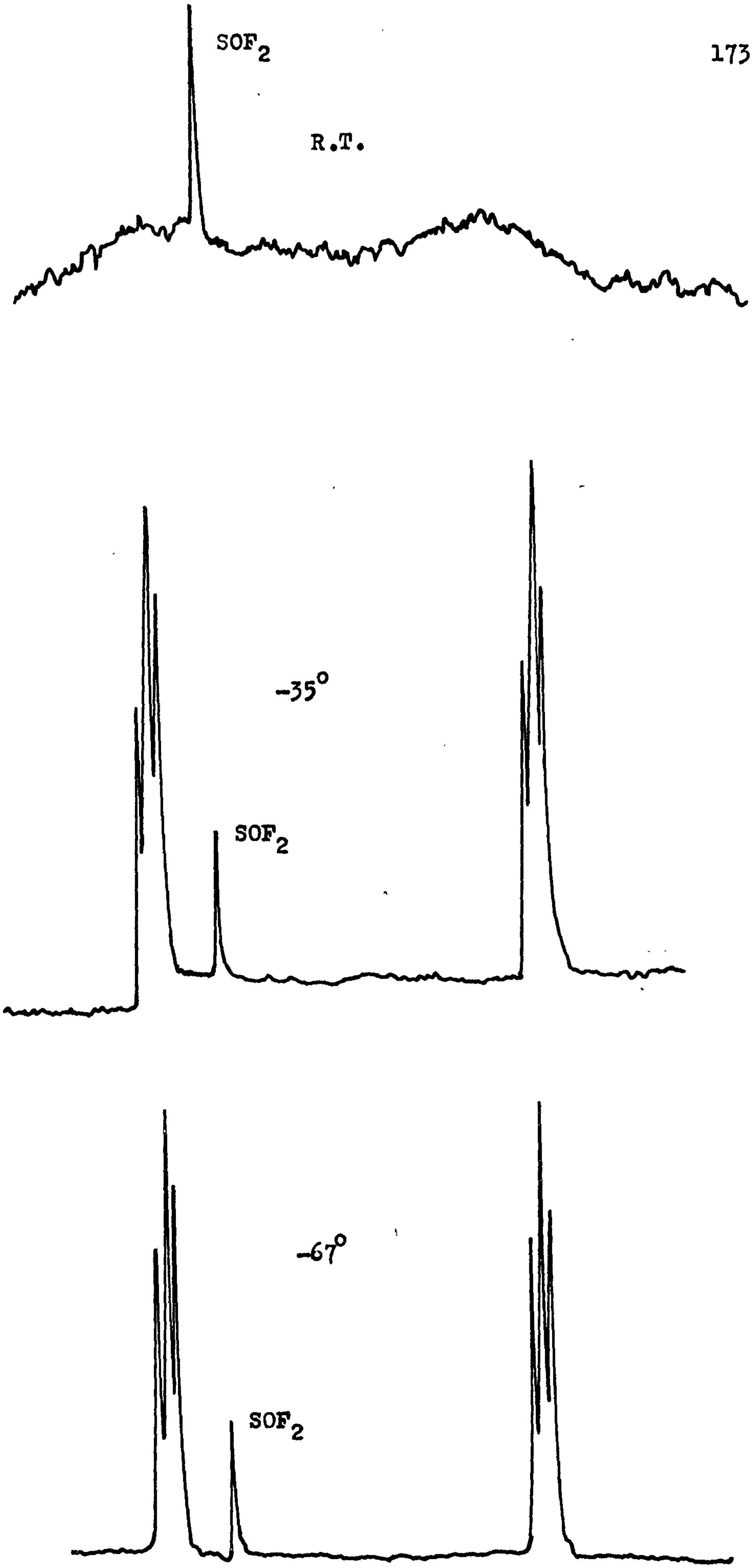
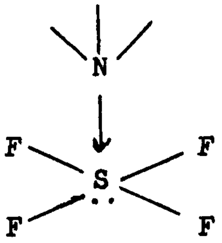


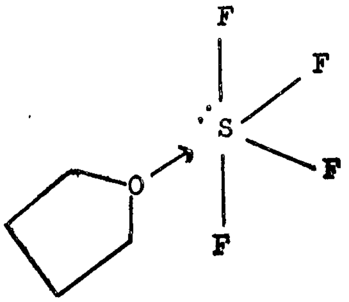
FIG.30- F^{19} N.M.R. Spectra of SF_4-THF.

the adduct has the following square pyramidal structure



They also studied the SF_4 - THF system, but did not find any evidence for adduct formation, nevertheless they did observe that the fluorine exchange was slowed down. Muetterties, et al. did not report the temperature at which the fluorine NMR spectrum was examined.

In the present work the splitting of the fluorine resonace signal of SF_4 into two sharp triplets was observed at -25°. The chemical shifts at -40° and -67° were found to be 47.1 ppm and 45.3 ppm respectively and the coupling constant was found to be 66.4 cps. On the basis of these observations it is suggested that SF_4 and THF form a (1:1) molecular complex which is stable at low temperatures. Since the fluorine resonance spectrum of the adduct is composed of two triplets the following structure is proposed for the complex:



The difference in the structures of $SF_4.N(CH_3)_3$ and SF_4.THF is interesting, but not easy to account for.

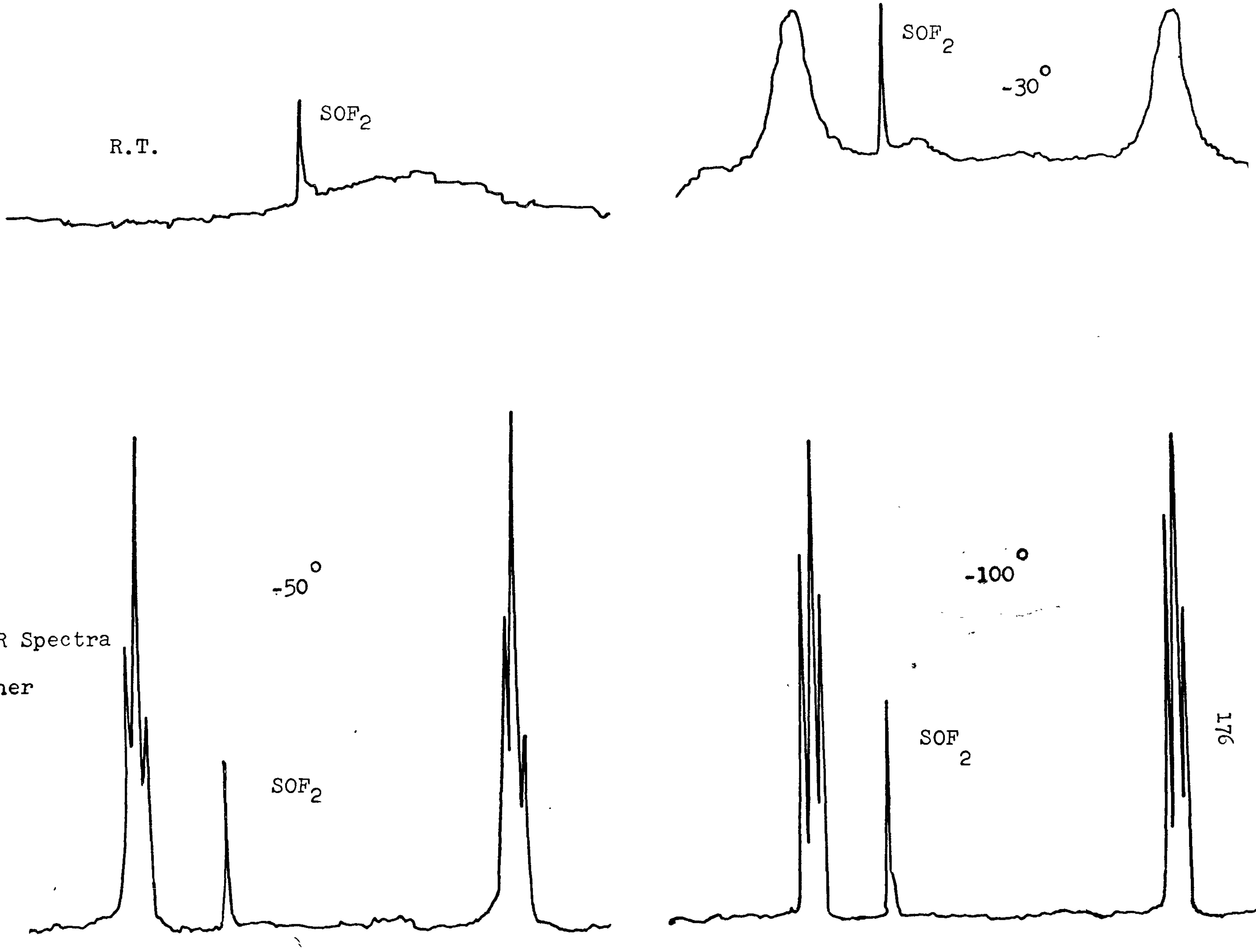
SF_4 - Ether System: Fluorine Nuclear Magnetic Resonance

Since ether also forms adducts with Lewis-acids 172,173) the fluorine NMR spectrum SF_4 - Et_2O system was also examined. The sample for NMR measurement was prepared in the same manner as the THF - SF_4 sample. The sample did not show any visible change when kept at room temperature for two or three days.

The F^{19} NMR spectrum of SF_4 - Et_2O was observed, between room temperature and -132°. At room temperature one very broad peak, about 1600 cycle wide, was observed which split into two broad peaks at -5°. As the temperature was lowered the two peaks narrowed. At -35° these peaks showed a triplet structure which became well defined at -45°. The shape of the spectrum did not change down to -132°, however, the two triplets came closer together. The NMR spectra of SF_4 - Et_2O at room temperature, -30°, -50° and -100° are shown in Fig.31. The chemical shifts between the two triplets and the coupling constants at different temperatures are given in Table 31. The average coupling constant was found to be 74.3 which is about two cycles less than that of pure SF_4.

Discussion

In trigonal bipyramidal molecules the axial bonds are longer than the equatorial bonds 135). Muetterties, et al. 175) have reported that in trigonal bipyramidal molecules, e.g. PF_5, R_2 PF_3 etc. the coupling constant J_{PF} for the axial bond is smaller than that of the



IG.31- F^{19} NMR Spectra of SF_4— Ether equatorial P-F bond. The interaction between SF_4 and a nucleophile viz: ether and THF etc. would cause the electron density on the S atom of SF_4 to increase which would probably in turn result in lengthening of the S-F bond. The small difference between the coupling constant of SF_4 and that of SF_4-Et_2O shows that the S-F bond lengths in SF_4-Et_2O are not much different from those of SF_4. It is, therefore, suggested that the interaction between SF_4 and ether is weak. However, the appreciable decrease in the fluorine-fluorine coupling constant of the SF_4-THF system indicates that the S-F bonds in SF_4 - THF are probably longer than S-F bonds in SF_4, indicating a stronger interaction between SF_4 and THF. The fact that the F^{19} resonance signal of SF_4 - THF splits up into two resonances at a higher temperature than that of SF_4 - Et_2O (Figs. 30 and 31) also indicates that the interaction between SF_4 and THF is stronger than between SF_4 and ether. The foregoing conclusion is consistent with the fact that THF is more basic than ether 172,173).

Recently Muettertie 67) has reported cis and trans isomer complexes of the metal (IV) fluorides such as TiF_4, ZrF_4 and SnF_4 etc., but so far this type of isomerism has not been reported for the complexes of sulphur group tetrafluorides. It is suggested that an NMR study of MF_4(M = S, Se or Te) solutions in amines and amides of varying strength would provide conclusive evidence regarding the cis and trans complexes of SF_4, SeF_4 and TeF_4.

The solubility of SF_4 in tetrahydrofuran and diethyl ether

The decomposition of the labelled complex $SF_4.BF_3$ with tetrahydrofuran and ether has been described in Chapter 5. Before commencing the tracer study it was considered necessary to determine the approximate solubilities of SF_4 in these solvents at ambient temperature. The solubility was determined by bubbling the gas through the anhydrous solvent long enough to obtain a saturated solution. The solution was then analysed for SF_4.

Procedure

The apparatus used is shown in Fig.32. The part of the apparatus on the left of the dotted line (Fig.32) was dried at 150°. The bubblers B_1 and B_2 contained sodium hydroxide solution (10 per cent). By means of the separating funnel (Fig.32) 25 mℓ of the solvent were run into the reaction vessel and SF_4 was bubbled through the solvent at the rate of 2 bubbles per second. After twenty minutes the SF_4 was cut off and a fast current of purified nitrogen was passed through the apparatus for a few minutes to sweep out the SF_4 accumulated in the space above the solvent in 'A' (Fig.32). In this operation it is expected that a little SF_4 will be lost, but the error in the solubility is expected to be very small. The bubblers B_1 and B_2 were disconnected and A was cooled in an ice bath. Then 10 mℓ of an ice-cold sodium hydroxide solution (16 per cent) were slowly added to the SF_4 solution in 'A' and the tube was shaken vigorously to completely absorb the hydrolytic products of SF_4. The solution was heated on a steam bath to voltalize the excess solvent. After cooling to room temperature the solution was diluted to 250 mℓ. A 25 mℓ portion of this solution was taken for the determination of SF_4 via $BaSO_4$.

The solubilities of SF_4 in ether and tetrahydrofuran at room temperature found in the manner are given below:

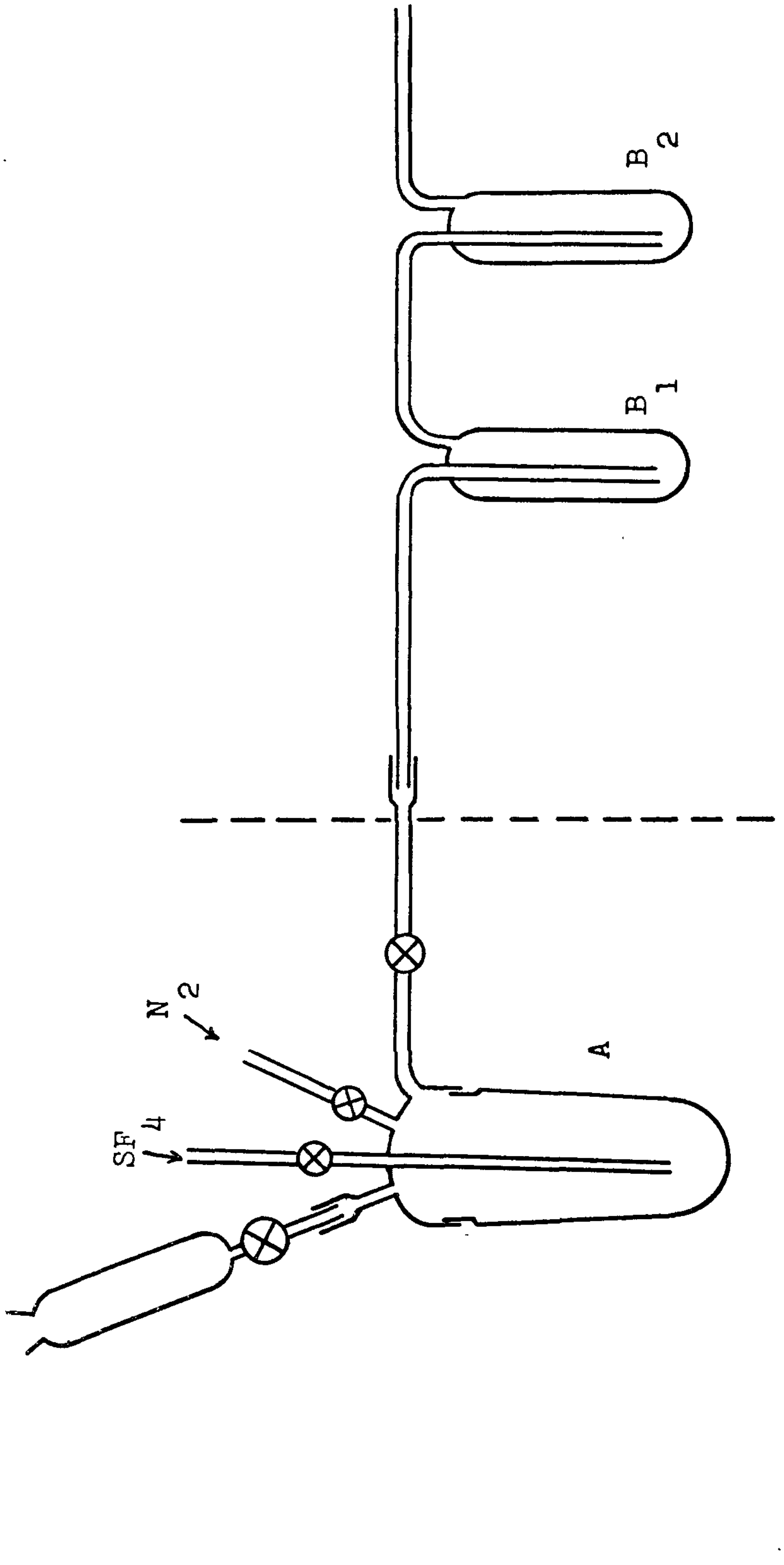


FIG.32

SOLVENT	Weight of SF_4 in g./100 g. of SOLVENT
Ether	1.77
Tetrahydrofuran	3.38

It is suggested that the dissolution of SF_4 in ether and THF is the result of weak acid-base interaction. It has been shown that THF is a stronger base than ether$^{172,173)}$. Thus the interaction between SF_4 and THF will be stronger than between SF_4 and ether and consequently it is expected that SF_4 will be more soluble in THF than in ether.

SeF_4 - Et_2O System: Fluorine Nuclear Magnetic Resonance

The fluorine nuclear magnetic resonance spectrum of liquid SeF_4, consists of a single peak. Muetterties$^{6)}$ studied the NMR spectrum of an SeF_4 solution in propane at low temperatures. At about -200° two fluorine resonances were observed, which broadened and merged when the temperature was raised above -190°. The fluorine resonances could not be resolved into the expected triplets because it was not possible to cool the sample below -200°. Samples of SeF_4 - THF and SeF_4 - Et_2O were prepared in the same manner as for SF_4 - THF. The SeF_4 - THF sample decomposed as soon as it was warmed to room temperature, but the SeF_4 - Et_2O sample remained unchanged for about twenty hours. The SeF_4 - Et_2O sample could be stored for several weeks at -80°. The NMR spectrum of a freshly prepared sample of SeF_4 - Et_2O showed a broad peak at room temperature. The peak narrowed a little as the temperature was lowered, at -105° it was three-fourths as broad as at room temperature. Below -105° the

F^{18} resonance signal disappeared indicating that the sample had solidified. Since SeF_4 is a weak Lewis acid[14, 40, 41] it would interact with diethyl ether. It is, therefore, suggested that inspite of a weak interaction between SeF_4 and ether the intra molecular fluorine exchange is fast. However, the interaction between SeF_4 and tertiary amines, e.g. C_5H_5N and $(CH_3)_3$ N etc. might be expected to be stronger than the interaction between SeF_4 and ether and F^{19} NMR spectra of these systems would be interesting to investigate.

CHAPTER 9

Miscellaneous Experiments

Fluorine-18 Exchange between LiF^{18} and SOF_2

Recently Ruff and Lustig$^{63)}$ postulated the existence of an ionic complex of SOF_2, namely $CsSOF_3$. If this type of intermediate or compound exists it is a logical conclusion that fluorine-18 would exchange between LiF^{18} and thionyl fluoride. Therefore, the exchange reaction was carried out as described below.

Labelled lithium fluoride was prepared as described earlier. Purified SOF_2 (about 500 mℓ at am. press) was condensed on dry LiF^{18} and then warmed to -45° to -50°. It was maintained at this temperature for one half-life of F^{18} and then distilled under vacuum, into a receiver cooled to liquid air temperature. The distillate was hydrolysed with sodium hydroxide solution (16 per cent) and counted for F^{18}. The count rate of the thionyl fluoride was found to be of the order of 10^4 cpm/g. of thionyl fluoride.

Discussion

The exchange of F^{18} between LiF^{18} and SOF_2 indicates that SOF_2 is a Lewis-acid like SF_4. The formation of $CsSOF_3$ has been suggested by Ruff and Lustig$^{63)}$. It is, therefore, suggested that fluorine exchange in the system LiF^{18} - SOF_2 takes place via an unstable intermediate $LiSOF_3^{18}$. The instability of $LiSOF_3$ is due to the small size and high polarizing power of Li^+ and relatively weak acceptor strength of SOF_2.

Ruff and Lustig63) have also suggested the formation of $CsSOF_5$. If such a compound is formed exchange of F^{18} should be observed between LiF^{18} and SOF_4.

Further, on the basis of the above discussion we suggest that it should be possible to prepare $(CH_3)_4NSOF_3$ and $(CH_3)_4NSOF_5$ and that these compounds would be **at least** as stable as $(CH_3)_4NSF_5$ 22). The postulated adducts of SOF_2 and SOF_4 with $(CH_3)_4NF$ could be used for preparing highly pure SOF_2 and SOF_4 by reacting the adducts with boron trifluoride. Boron trifluoride would form $(CH_3)_4NBF_4$ 8) and the thionyl compound will be set free.

Solubility of lithium fluoride in organic solvents

About two years ago Tunder and Seigel22) proved the existence of the SF_5^- anion by preparing $(CH_3)_4NSF_5$, although the salts of this anion with simple metal cations such as Cs^+, K^+ etc., are unstable22). As a result of this investigation and the preparation of SF_4^{18} from LiF^{18} (Chapter 3) it was proposed to study the exchange of fluorine between LiF and SF_4 in an inert solvent such as acetonitrile, dimethyl formamide (DMF), dimethyl sulfoxide (DMS) and tetrahydrofuran etc. employing fluorine nuclear magnetic resonance spectrometry. In order to undertake this investigation it was necessary to know the solubilities of LiF in these solvents. Lithium fluoride has been reported to be sparingly soluble in water176) and THF[177) and practically insoluble in nitrobenzene[178), benzene acetone,[176,178) toluene, dioxane, hydrazine[178), ether[177) and DMS[179).

The solubility of LiF in THF, 0.6 per cent w/w, seemed to be promising for our purpose. However, 100 mg of LiF did not dissolve in 25 mℓ of THF even on warming and shaking for several hours. This observation necessitated the redetermination of the solubility of LiF in THF. In addition, the solubility of LiF was also determined in acetonitrile, DMF, DMS and nitromethane. Because the solubilities of LiF in these solvents appear to be far below the weighable limits it was necessary to use a very sensitive technique.

The solubility of LiF in water at 25° [176) was taken as standard and the solubility of LiF in the organic solvent was determined by comparing the activity of LiF^{18} in aqueous solutions with the activity of LiF^{18} in nonaqueous solutions.

Procedure

Lithium fluoride labelled with fluorine-18 was prepared by dissolving irradiated lithium carbonate in dilute hydrofluoric acid, (Chapter 3). About 10 mℓ of each of the anhydrous organic solvents and 10 mℓ of water were taken in a dry glass stoppered conical flasks. To each flask about 0.2 g. of dry LiF^{18} was added and the solutions were shaken for one hour, and then filtered. Since the radioactivity of the aqueous solution was very high as compared to that of non aqueous solutions, 5 mℓ of the aqueous solution of LiF^{18} were diluted to 100 mℓ. Five mℓ of the diluted aqueous solution and 5 mℓ from each of the non-aqueous solutions were taken to determine the F^{18} activity. Each solution was counted several times over a period of two half-lives of fluorine-18, and the count rate of each solution calculated at some convenient time. The solubility of LiF in the organic solvents was calculated from the following expressions

$$\frac{N_1}{W_1} = \frac{N_2}{W_2} \qquad (1)$$

$$S = W_2 \times \frac{20}{d}$$

where

S = Solubility of LiF.

N_1 = Number of counts for aqueous solution of LiF^{18}.

W_1 = Weight of LiF^{18} in aqueous solution; calculated from the solubility.

N_2 = Number of counts from non aqueous solution.

W_2 = Weight of LiF^{18} in non aqueous solution.

d = Density of organic solvents.

The results of this investigation are summarized in Table 32.

The tracer technique for the determination of solubility is extremely sensitive as compared to other physical methods. The solubility of LiF in THF reported earlier is certainly wrong.

TABLE 32

Solubility of LiF at room Temperature (25°)

Solvent	Solubility Reported	LiFg/100 g. solvent Tracer Method		Disintegration per minute in 5 mℓ	
		I	II	I	II
Water	0.133 176)	-	-	7400	14542
Dimethyl formamide	-	0.52×10^{-4}	1.20×10^{-4}	55	249
Dimethyl sulfoxide	0.0 179)	1.00×10^{-3}	2.27×10^{-3}	559.6	545
Acetonitrile	-	0.87×10^{-4}	1.27×10^{-4}	75	216
Nitro methane	-	0.64×10^{-5}	1.62×10^{-5}	10	49
Tetrahydrofuran	0.6 177)	1.85×10^{-5}	1.34×10^{-5}	18.2	26

Polymerisation of Tetrahydrofuran by SF_4

In 1960 Meutterties reported the polymerisation of THF by PF_5 at temperatures between 10° and 30° 45). The material obtained was a white rubbery solid, and had a melting point in the range 150° - 215° 45).

Sulphur tetrafluoride has been reported to be a very good fluorinating agent 16,17), but not a polymerising agent. However, in connection with the NMR study of the SF_4-THF system a tube containing the sample which had become viscous was accidently broken. It was quickly immersed in water in order to destroy SF_4. Surprisingly enough, the viscous liquid was transformed into an opaque rubbery solid. The solid was washed for several hours in cold water and then air dried. The polymer has remained unchanged at room temperature, for at least two and a half years.

The wt/wt solubility of the polymer in THF and in acetone was found to be 30 per cent and 0.5 per cent respectively. The polymer could be recovered from the THF solution by adding water. The specific gravity of the polymer was determined by the water displacement method and was found to be 0.5.

The polymer was analysed for fluorine by the following procedure: About 0.1 g. of the polymer was fused with an equal weight of clean sodium metal at low temperature and then heated to redness. The red hot fusion tube was quenched in about 5 mℓ of distilled water, and the solution was boiled and filtered. The filtrate was neutralized with HCℓ. To neutral solution were added 2 mℓ of saturated solution of $LiCl$ in ethanol. Then alcohol was added to the solution until the concentration of ethanol in the liquid phase became 50 per cent[126)] by volume. The solution was shaken vigorously and allowed to stand for several hours, but no precipitate (LiF) or turbidity could be observed. The absence of fluorine in the polymer showed that it was simply a polymer of THF and therefore it is concluded that SF_4 can behave as a polymerising agent.

CHAPTER 10

Conclusion

In this chapter the results of the investigations described in the preceding chapters are summarized and possible applications of F^{18} are discussed.

A number of fluorides have been labelled by exchange with LiF^{18} either in the gaseous or the liquid phase.

The results of the F^{18} investigations of the adduct $SF_4.BF_3$ are consistent with a fluorine bridge structure (Fig.10) and so is the vibrational spectrum of the complex. However, the fluorine-19 nmr spectrum of a solution of $SF_4.BF_3$ in HF indicates that the compound is ionized into SF_3^+ and BF_4^-. Presumably the ions are stabilised by solvation by HF.

It has been shown unequivocally by the F^{18} tracer method that the compounds $SF_4.PF_5$ and $SF_4.AsF_5$ do not have the simple co-ordinate bond structure.

The formation of a (1:1) complex between SF_4 and SiF_4 was indicated by the tracer study. The formation of the $SF_4.SiF_4$ and $SiF_4.(SF_4)_2$ adducts was confirmed by the infra-red spectrum. It has been suggested that interaction between SiF_4 and SF_4 takes place through fluorine bridges

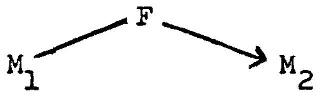
The investigation of the POF_3 - BF_3 system confirmed the results of Booth and Walkup. The tracer study has shown that in the complex $POF_3.BF_3$ bonding through oxygen is not likely. A covalent structure involving fluorine bridge has been proposed for the adduct $POF_3.BF_3$.

In connection with the investigation of the SiF_4 - SF_4 system an analytical method was developed for the determination of sulphate in the presence of soluble compounds of silica. From this study it has been concluded that SiO_3^{2-} is capable of complexing with strong nucleophiles such as dimethyl formamide and the complex is stable in strongly acidic medium.

It has been found that SF_4 forms (1:1) addition compounds with diethyl ether and tetrahydrofuran, and the latter is also polymerised by SF_4.

Fluorine Bridge

The fluorine bridge involves the donation of a pair of electrons from a bonded fluorine atom to another atom, i.e.



This bonding can formally be regarded as the formation of two bonds by a F^+ ion. The electron density about the bridging fluorine atom would be expected to be lower than that for the same fluorine atom without bridging. The interaction between the donating fluorine and M_2 would depend upon the acceptor strength of M_2. Thus an asymmetric fluorine bridge may be observed where the interaction is either relatively strong or weak.

The fluorine bridge is not common, it has been observed in compounds which are associated. The F^{19} NMR spectrum of SbF_5[180)] shows fluorine bridging in the liquid and the X-ray crystal structures of MoF_5[181)] and RuF_5[182)] show that both compounds exist as fluorine bridged tetramers. Fluorine bridging has also been suggested for the system AsF_3-SbF_5[183)]. Recently examples of fluorine bridging between two different elements have been provided from the vibrational spectra of the complexes $SeF_4.BF_3$, $SeF_4.AsF_5$ and $SeF_4.SbF_5$ etc.[136)].

Possible Applications of Fluorine-18

Considering the evergrowing importance and wide and varied applications of fluorine and its compounds, the use of fluorine-18 in the chemistry and technology of this element has been quite insignificant. Nevertheless, it could probably be employed for solving a vast number of problems. Some possible applications of F^{18} are suggested in the following discussion.

This isotope may be used in connection with fundamental studies involving the chemistry of freons which are used extensively as refrigerants. Labelled freons may be readily prepared by fast neutron bombardment (Table 4) of the appropriate compounds.

The fluorine containing polymers teflons and Keℓ-F are distinguished by their chemical inertness, thermal stability and other physical characteristics. A number of interesting properties of these polymers such as solubility in various solvents, disintegration in intense γ-rays flux, decomposition at elevated temperatures and frictional properties could be studied by employing F^{18}. Teflons or Keℓ-F can be readily labelled with F^{18} by bombarding the polymer with fast neutrons or by exchanging fluorine with a labelled fluoride such as HF^{18} or $C\ell F_3^{18}$ etc.

The solubility of the polymer may be determined by making a saturated solution of the labelled polymer in the desired solvent followed by counting of F^{18} in a known volume of the solution and determining the specific activity of the test sample separately. From these two sets of data the solubility of the polymer can be calculated.

Teflons are frequently used in devices which are exposed to intense γ-radiation. To determine the effect of large and intense doses of γ-radiation on the polymer, the test sample could be labelled with F^{18} and exposed to γ-rays for a predetermined period. After irradiation the test sample could be analysed by liquid or gas phase radiochromatography or any other radiochemical technique to identify the fluorocarbons produced during the irradiation.

Teflons are frequently used for making moving parts of certain specialised and precision equipment. In designing such gadgets a knowledge of frictional properties, and malleability etc. is important. To determine these properties the machine may be fitted with F^{18} labelled teflon parts. Then the machine is run for predetermined period and the change in F^{18} activity in the test parts is determined. From the counting data, after correcting for decay of F^{18}, information on the above mentioned properties may be obtained.

Ionic equilibria involving fluorine in both aqueous and non-aqueous media can be studied with fluorine-18. Thus it would require only a straightforward application of tracer methods to measure the ionic mobility of F^- in solvents such as HF etc. with F^{18}. Similarly it should be possible to obtain valuable information concerning the formation of fluorine-containing complex compounds.

At present no simple and completely satisfactory analytical method for the determination of fluorine is known. Because of its easily detectable activity, F^{18} may be of use in this connection in several ways. First, the method of isotopic dilution could be applied to this determination, second, F^{18} can be used as tracer to aid in the evaluation of any proposed new analytical technique such as precipitation, complex formation and ion exchange.

To use F^{18} as a tracer in the development of better analytical methods one needs only to study the relative efficiency of a separation procedure as the experimental conditions are changed working from aliquots of a stock solution of labelled fluorine ion. This technique is ideally suited to studies of ion-exchange methods of separation, using conventional tracer techniques for the evaluation of the resin capacity, the rate of up-take, and the rate of elution of fluoride ion.

Solubilities of a large number of fluorides in anhydrous HF are known184). Studies of this kind might well be extended to substances of considerable lower solubility and to lower temperatures by the use of F^{18} labelled compounds. Rates of dissolution might be measured by taking advantage of the convenient gas phase radio-assay of HF^{18} provided the rate of equilibration of F^{18} between liquid and the gaseous HF was greater than the rate of dissolution.

When water is fluorinated it is necessary to measure the concentration of fluoride ion in the range of parts per million with considerable accuracy. Here also F^{18} might prove to be a useful tool in controlling the rate of additions of fluorinating agent.

CHAPTER 11

Experimental

Infra-red Spectroscopy

The infra-red spectra were taken with a reflection grating type infra-red spectrometer - Perkin Elmer - Model 521. Apiezon T grease was used to seal the windows to the cell and Keℓ-F grease was used for the joint between the cell and the sample holder.

Silver chloride windows were used to obtain the spectra of the compounds between 500 cm^{-1} and 2100 cm^{-1}. A compensating window was placed in the reference beam, and the cell was further balanced by partially closing the reference beam of the spectrometer.

Polyethylene windows were used to obtain the spectra between 600 and 250 cm^{-1}. The windows were made of 3/16 inch thick polyethylene discs. Compensating windows made of the same polyethylene, were placed in the reference beam and the cell was further balanced by partially closing the reference beam window of the spectrometer.

The polyethylene windows buckled slightly under vacuum. Therefore, it was necessary to apply pressure around the edge of the window in contact with the cell. This was accomplished with the clamp shown in Fig.14.

F^{19} NMR Spectroscopy

The NMR spectra of the fluorine compounds were taken at 56.4 Mc/s and 14000 gauss employing a Varian High Resolution NMR Spectrometer, Model 4300B.

Determination of Chemical Shifts with respect to a Standard

Chemical shifts of the order of a thousand cycles were measured by the side-band method185). The fluorine-19 resonance signal of the sample under investigation was brought to the center of the scope. The test sample was then replaced by the 'standard' and the frequency of the audio-modulation was increased until the first side-band of the standard's signal was brought to the centre of the scope. The frequency of the modulating signal was a measure of the chemical shift of the test sample with respect to the standard.

When the chemical shifts were greater than 1000 cps the following procedure was adopted. The resonance signal of the test sample was recorded on the chart. Without disturbing the settings of the spectrometer the sample was quickly replaced by the standard and its resonance signal was recorded. A modulation of suitable frequency was applied to the resonance signal of the standard. The first side-band and the signal were recorded on the chart and this separation was used to calculate the chemical shift of the test sample with respect to the standard. The sweep rate was adjusted so as to allow enough time for interchanging of the samples.

Preparation of Low-Temperature Bath

For preparing low-temperature baths between 0° and -80°

usually acetone, chloroform or CCl_4 and dry ice are used. In the present investigation low-temperature bath at -130° was often required. It was prepared from n-pentane and liquid air. Cooling of n-pentane by direct addition of liquid air is hazardous. The arrangement shown in Fig.33 was employed for cooling n-pentane.

The low-temperature bath could be warmed by passing a fast current of air through a U tube immersed in the bath.

Cold Funnel

For cooling liquid reagents to temperatures below a separating funnel coaxially sealed to a Dewar flask (Fig.34) was used.

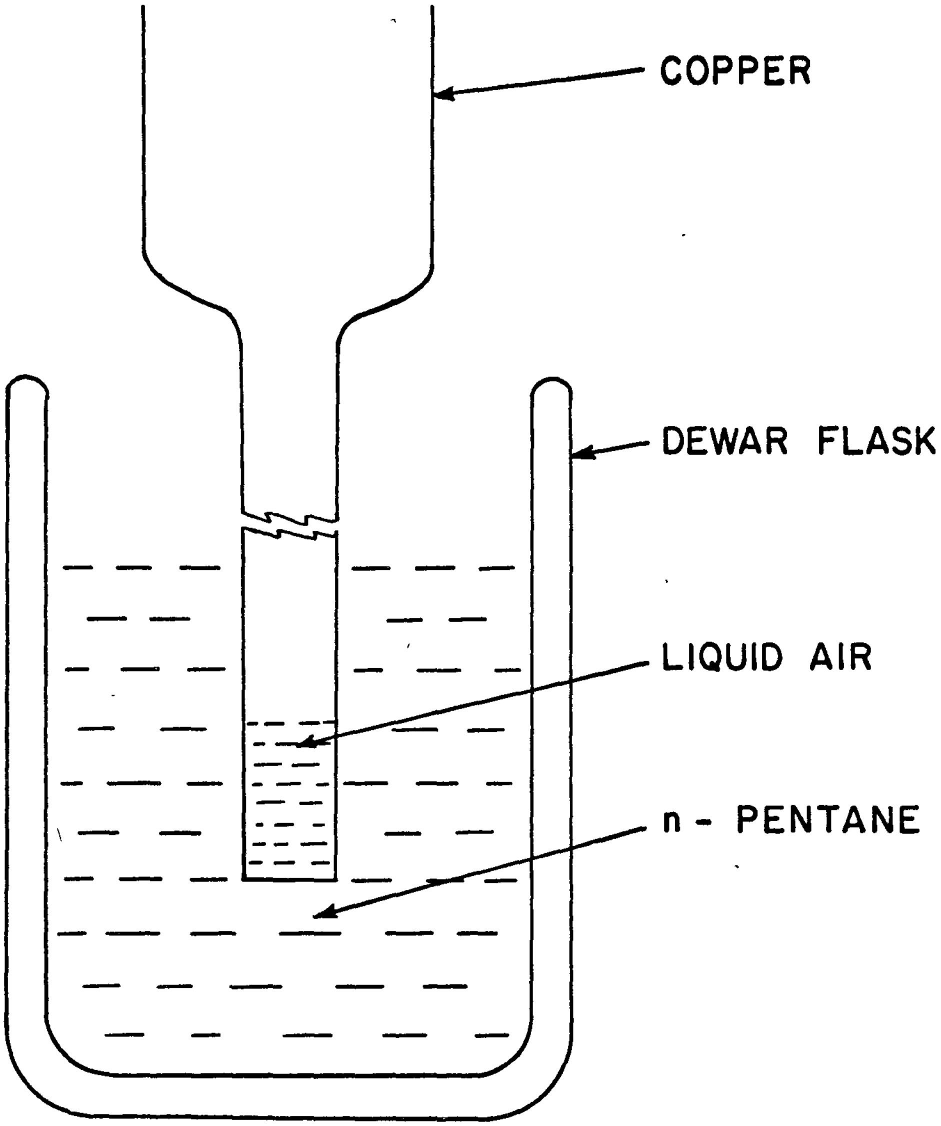
Reagents

All the reagents used in this work were of A.R. quality. Some of the special reagents have been mentioned below.

Lithium Carbonate

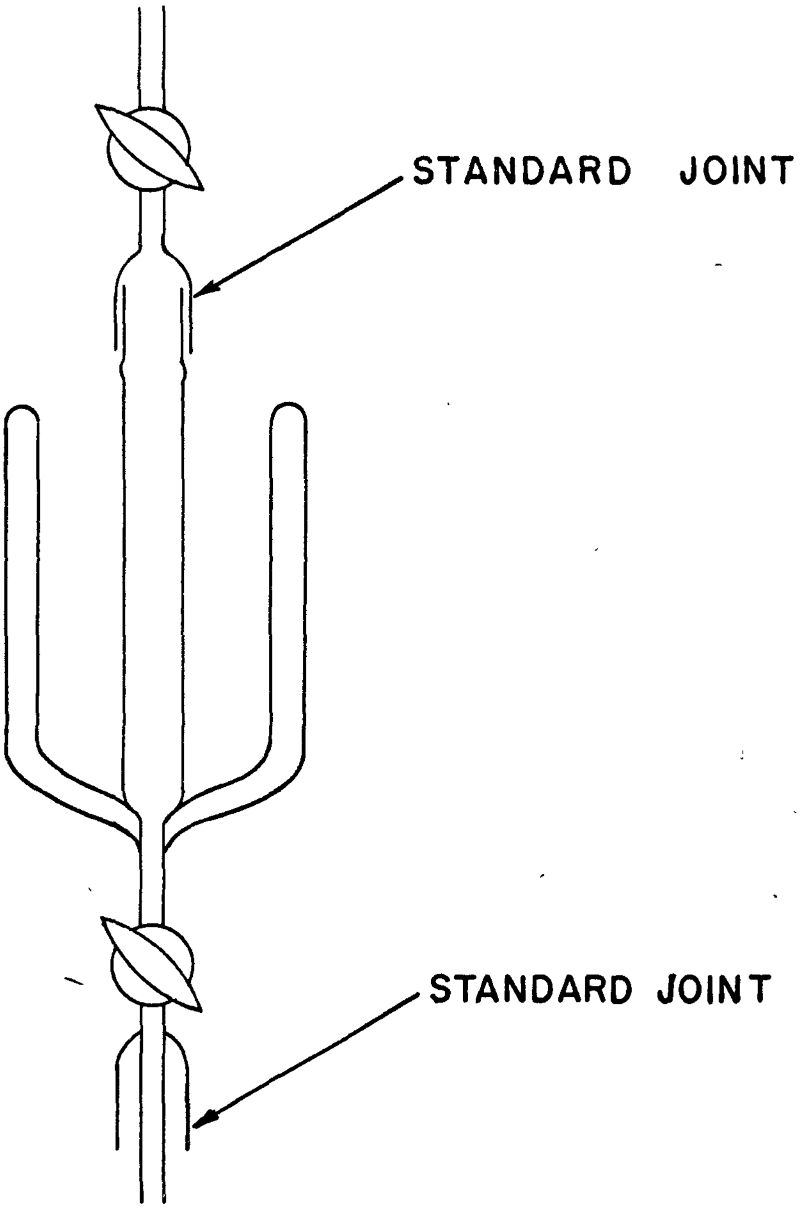
For the preparation of F^{18} Baker's analysed lithium carbonate of highest purity was used. The following table gives the percentage of various impurities in the reagent.

Cl	0.000
N compounds (as N)	0.003
SO_4	0.21
Heavy metals as Pb	0.001
Ba	0.000
Other alkalies (as Cl)	0.20
Fe	0.000



ARRANGEMENT FOR COOLING n - PENTANE

FIG:33



COLD FUNNEL

FIG. 34

Sulphur tetrafluoride, silicon tetrafluoride, phosphorus pentafluoride and boron trifluoride were obtained from the Matheson Company. The SF_4 contained an appreciable quantity of $SC\ell_2$. This impurity was removed by slowly bubbling the gas through mercury[148)]. Each of these substances was further purified by vacuum distillation.

Arsenic pentafluoride and POF_3 were supplied by the Ozark Mahoning Company. They were purified by vacuum distillation.

Selenium tetrafluoride was prepared by passing fluorine gas, diluted with purified nitrogen, over sublimed selenium at 0°. The reaction took about eight hours to complete. The selenium tetrafluoride contained a little unreacted selenium in suspension. It was purified by vacuum distillation and then sealed in a glass tube with a break-seal.

Thionyl fluoride was prepared by fluorinating $SOC\ell_2$ with SbF_3 at 125°- 150° in the presence of $SbC\ell_5$ (catalyst)[61)]. Thionyl fluoride was purified by distilling at -100° to -105° under vacuum. The NMR spectrum of the purified substance consisted of a single sharp peak which coincided with SOF_2 peak from a known sample.

Preparation of the Ammonium Molybdate Reagent[129)]

The ammonium molybdate reagent was prepared as follows: Ammonium nitrate solution was made by dissolving 125 gms of the salt in 125 mℓ of water and 175 mℓ of concentrated nitric acid and 12.5 gms of A.R. ammonium molybdate were dissolved in 75 mℓ of water. The ammonium molybdate solution was added slowly with constant stirring to the ammonium nitrate solution. The resulting solution was diluted to 500 mℓ with water and then kept on a water bath at 60° for six hours. Then the solution was filtered through a Whatman No.42 filter paper to remove the small amount of precipitate. This reagent had good keeping qualities, no formation of precipitate was observed even after several weeks.

Radiation Protection

The handling of radioactive material requires the use of special precautions for personal protection. In this work the tracer amounts of F^{18} used were sufficiently low that they could be handled in an ordinary chemical laboratory using standard radiochemical techniques186).

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