ARSENIC TRIFLUORIDE - SULPHUR TRIOXIDE MIXTURES

A STUDY OF ARSENIC TRIFLUORIDE - SULPHUR TRIOXIDE MIXTURES BY F^{19} NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

By

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SCOPE AND CONTENTS: A liquid obtained by distillation from mixtures of arsenic trifluoride and sulphur trioxide which was supposed to have the composition $2AsF_3.3SO_3$ has been regarded as a definite chemical compound for which several structures have been proposed. The reaction between arsenic trifluoride and sulphur trioxide has been reinvestigated using F^{19} n.m.r. spectroscopy, vapour-density measurements and cryoscopy in fluorosulphuric acid. Evidence has been obtained for the formation of the new compounds $AsF_2(SO_3F)$, $AsF(SO_3F)_2$ and $As(SO_3F)_3$, although none of these have been obtained pure. The supposed compound $2AsF_3.3SO_3$ is in fact a constant-boiling mixture which does not have exactly this stoichiometric composition and whose composition varies with the pressure. In mixtures containing an excess of sulphur trioxide polysulphuryl fluorides $S_nO_{3n-1}F_2$ are formed in substantial amounts.

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CHAPTER 1 INTRODUCTION

(i) The Supposed Compound $2AsF_3.3SO_3$.

In 1955, Engelbrecht, Aignesberger and Hayek (1) reacted sulphur trioxide with arsenic trifluoride, with either reactant in 20 per cent excess. They had expected to obtain, as products of the reaction, disulphuryl fluoride, $S_2O_5F_2$, and an oxysulphate of arsenic, $As_2O(SO_4)_2$, by analogy with the reaction of sulphur trioxide with antimony pentafluoride (2) which does produce disulphuryl fluoride and for which they wrote the following equation:

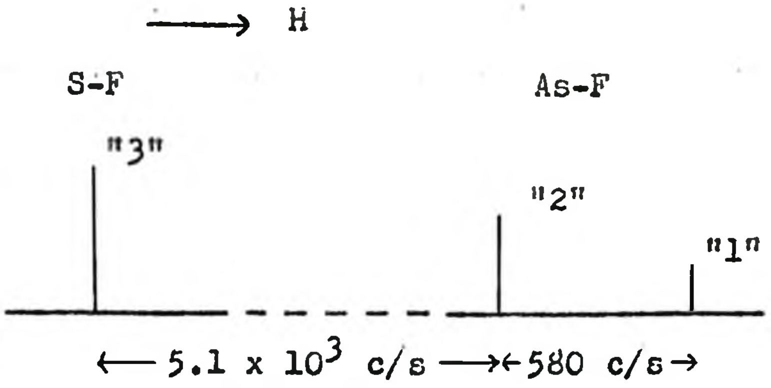
$$[1] \quad 2SbF_5 + 14SO_3 \longrightarrow Sb_2O(SO_4)_4 + 5S_2O_5F_2.$$

The reaction between arsenic trifluoride and sulphur trioxide yielded neither disulphuryl fluoride nor the oxysulphate, but they obtained a liquid which boiled at 138°C./709 m.m. This was a colourless, volatile material soluble in sulphuryl chloride, SO_2Cl_2, disulphuryl chloride, $S_2O_5Cl_2$, fluorosulphuric acid and phosphorus oxychloride, but which hydrolysed and decomposed in water. They claimed that the same distillate was obtained whether the distillation was carried out under atmospheric or reduced pressure. By chemical analysis, it was found that this material had a composition consistent with the empirical formula $2AsF_3.3SO_3$:

Calc.: %As 29.73 %SO_3 47.65 %F 22.62
Found: 29.93, 29.81 47.51, 47.28 22.52, 22.25

Determination of the molecular weight by cryoscopic measurements in phosphorus oxychloride gave an average value of 200 instead of 504 as required by the empirical formula. As regards its structure they considered that a co-ordination complex $As(SO_3F)_3.AsF_3$, for which they did not specify the exact nature of the co-ordinate bond, was unlikely; and they suggested that it might have a structure based on the trimeric sulphur trioxide ring with two of the oxygen atoms co-ordinated to two electrophilic arsenic trifuloride molecules.

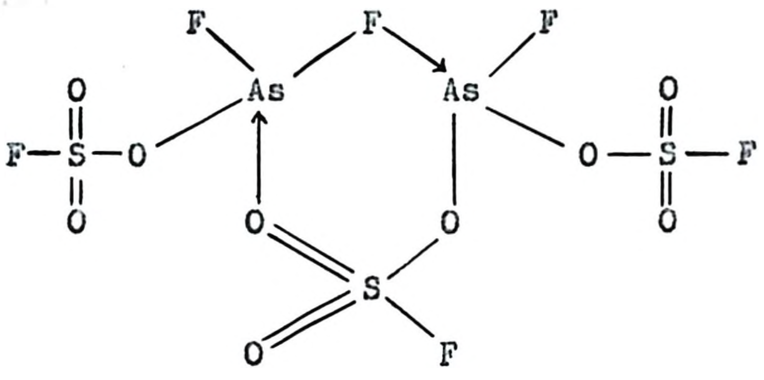
Then in 1958, use was made of F^{19} nuclear magnetic resonance spectroscopy in an attempt to elucidate the molecular structure of this supposed compound. Muetterties and Coffman (3) showed that the F^{19} nuclear magnetic resonance (n.m.r.) spectrum of the liquid consisted of three resonance peaks, with relative intensities in the ratio of 3:2:1. The peak of intensity "3" appeared in the region characteristic of fluorine bonded to sulphur, whereas the other two peaks appeared in the region characteristic of fluorine bonded to arsenic. The peak of intensity "2" was 5.1×10^3 cycles/sec. (c/s) to high field of peak "3", and peak "1" was at about 580 c/s at still higher field (Figure 1).



<u>FIGURE 1</u>: F^{19} n.m.r. Spectrum of $2AsF_3.3SO_3$ at 56.4 M c/s

At temperatures above 30°C. the two peaks in the fluorine-on-arsenic region broadened and merged.

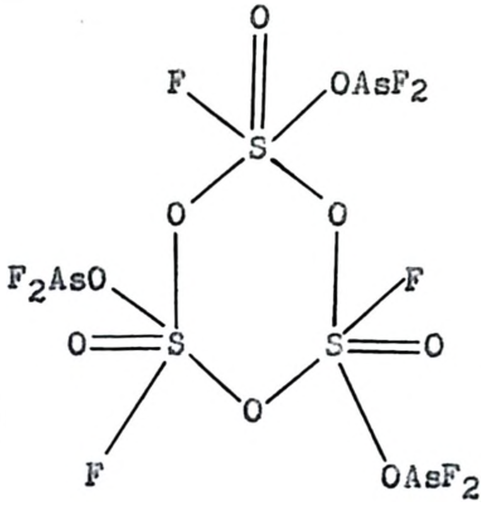
It is evident from the spectrum that there are two types of fluorine atoms bonded to arsenic, while the fluorine atoms bonded to sulphur are apparently all equivalent. To explain these results, they proposed the following structure:



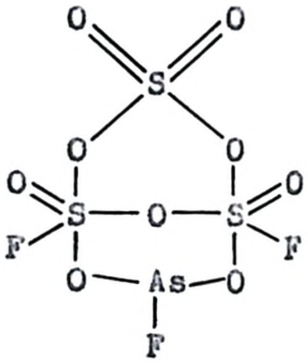
which is, in effect, a co-ordination complex of the two compounds $AsF_2(SO_3F)$ and $AsF(SO_3F)_2$. The fluorine atom, "bridging" across two arsenic atoms, was considered to undergo exchange with the other two fluorine atoms on arsenic, presumably by the breaking and re-formation of the co-ordinate bonds. The broadening and merging of the fluorine-on-arsenic signals with increasing temperature was attributed to an increased rate of exchange between the non-equivalent fluorine atoms.

The "bridging" fluorine atom is not equivalent to the other two fluorine atoms which are bonded to the arsenic atoms, and as they are separated from the "bridging" fluorine atom by two chemical bonds, it would be expected that fine-structure due to spin-spin coupling would be observed. Gillespie and Oubridge (4) estimated that the coupling constant would probably have to be 25 c/s or larger. However, no fine-structure was observed even at temperatures just above the melting point, $(-88^{\circ} \pm 2^{\circ}C)$. By studying the n.m.r. spectra of various arsenic trifluoride-sulphur trioxide mixtures in conjunction with the spectrum of the distillate $2AsF_3.3SO_3$, Gillespie and Oubridge proposed that a number of compounds in addition to $2AsF_3.3SO_3$ were formed and they suggested structures for these compounds based on the trimeric sulphur trioxide ring.

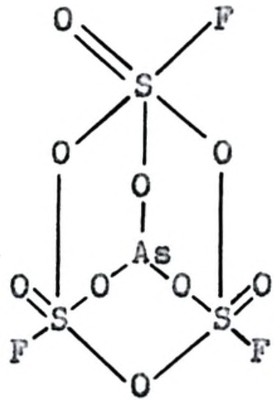
For the mixture with the mole ratio $AsF_3:SO_3 = 1:1$, the spectrum showed one fluorine-on-arsenic signal at 5.0×10^3 c/s to high field of the fluorine-on-sulphur peak, their relative intensities being $S\text{-}F/As\text{-}F = \frac{1}{2}$. The fluorine-on-arsenic peak was assigned to an $-OAsF_2$ group and the structure of the compound $AsF_3.SO_3$ that they supposed to have formed in this mixture was given as:



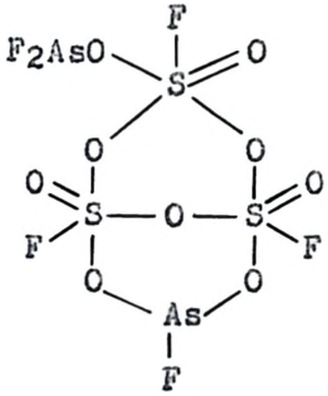
The spectrum for the mixture $AsF_3:SO_3 = 1:3$ also showed one fluorine-on-arsenic peak but in this case it was 5.5×10^3 c/s to high field of the fluorine-on-sulphur peak, and was only 1/6 as intense. This peak was assigned to an -OAsF.O- group. The relative intensities were explained by assuming the production of a mixture of two compounds in approximately equal amounts, which had the composition $AsF_3.3SO_3$ but were given the following structures:



and



The spectrum of the mixture of $AsF_3:SO_3 = 2:3$, in which all three peaks appeared, was very similar to that of the supposed compound $2AsF_3.3SO_3$; hence this compound was considered to contain both $-OAsF_2$ and $-OAsF.O-$ groups and to have the following structure:



(ii) General Reactions of Fluorides of Group V Elements and some other Elements with SO_3

The reactions of sulphur trioxide with the pentafluorides of Group VA elements (vanadium, niobium and tantalum) were reported by Clark and Emeleus (5) to follow the general equation:

[2] $$MF_5 + 2SO_3 \longrightarrow MF_3(SO_3F)2.$$

With niobium and tantalum pentafluorides, the reaction products could be formulated as $NbF_3(SO_3F)_2$ and $TaF_3(SO_3F)_2$ respectively, resembling the fluorosulphates $NbCl_3(SO_3F)_2$ and $TaCl_3(SO_3F)_2$ obtained from the reactions of niobium and tantalum pentachlorides with fluorosulphuric acid. With vanadium pentafluoride, the reaction products were disulphuryl fluoride and an oxyfluoride presumably formed by decomposition of the unstable fluorosulphate:

[3] $$VF_5 + 2SO_3 \longrightarrow VF_3(SO_3F)_2 \longrightarrow VOF_3 + S_2O_5F_2.$$

The reactions of sulphur trioxides with the trifluorides of Group VB elements were studied by Muetterties and Coffman (3). No reaction was observed with nitrogen trifluoride. The product with phosphorus trifluoride appeared to be a weak complex: $F_3P \longrightarrow SO_3$. The reaction with antimony trifluoride produced mainly the fluorosulphate $Sb(SO_3F)_3$.

Phosphorus pentafluoride did not react with sulphur trioxide (6) while antimony pentafluoride and sulphur trioxide reacted to give an oxysulphate and disulphuryl fluoride, as in Equation 1.

Muetterties and Coffman also studied the reaction between sulphur trioxide and alkaline earth metals (3). Calcium, strontium and barium fluorides react with two moles of sulphur trioxide to form reactive solids. These solids were shown to be ionic in character and dissolved in water to give solutions containing the fluorosulphate ion, and hence it was concluded that they were simple ionic fluorosulphates. Barium and strontium fluorosulphates decompose on pyrolysis to give sulphuryl fluoride and the corresponding sulphate

[4] $$M(SO_3F)_2 \longrightarrow MSO_4 + SO_2F_2.$$

Calcium fluorosulphate, however, decomposed on pyrolysis to give sulphur trioxide and calcium fluoride. But, if an excess of sulphur trioxide was used to react with calcium fluoride at 100° - 300°C and the resulting mixture treated with 60-98% sulphuric acid at 25°C, disulphuryl fluoride was obtained. A speculative sequence of reactions was given as follows:

[5] $$CaF_2 \xrightarrow{SO_3} Ca(SO_3F)_2 \xrightarrow{SO_3} Ca(S_2O_6F)_2 \xrightarrow{\text{excess } H_2SO_4} CaSO_4 + H_2SO_4 + S_2O_5F_2.$$

Trisulphuryl fluoride, $S_3O_8F_2$, was first obtained by Lehmann and Kolditz (7) from the reaction of gaseous boron trifluoride with liquid sulphur trioxide. This reaction yielded a white solid suspended in excess liquid sulphur trioxide. Addition of 70% sulphuric acid to the mixture gave rise to a layer of colourless oil from which trisulphuryl fluoride was obtained by distillation, boiling at 120°C. Gillespie, Oubridge and Robinson (8) later examined the F^{19} n.m.r. spectrum of this oil and found that the spectrum consisted of a number of signals each of which could be assigned to one of the members of an homologous series of polysulphuryl fluorides:

CHEMICAL SHIFTS*	0	-80	-109	-118	-123	-125.5
POLYSULPHURYL FLUORIDES	$S_2O_5F_2$	$S_3O_8F_2$	$S_4O_{11}F_2$	$S_5O_{14}F_2$	$S_6O_{17}F_2$	$S_7O_{20}F_2$

*Chemical Shifts from $S_2O_5F_2$ (internal) in c/s at 56.4 M c/s.

(iii) Aim of this Work

The aim of this work was to make a detailed study of the arsenic trifluoride-sulphur trioxide system, to obtain information on the supposed compound $2AsF_3.3SO_3$ and on other compounds that might be formed in this system. The most important method of investigation that was used was F^{19} nuclear magnetic resonance spectroscopy but useful information was also obtained from vapour-density measurements and from cryoscopic measurements in fluorosulphuric acid.

CHAPTER 11 EXPERIMENTAL METHODS - - APPARATUS AND MATERIALS

(1) Reagents

Baker and Adamson 30% fuming sulphuric acid was used as the source of sulphur trioxide which distilled at 44.5°C. Arsenic trifluoride was obtained by distilling the commercial product obtained from the Ozark-Mahoning Co. The boiling point of the arsenic trifluoride was 58°C.

(ii) AsF_3-SO_3 Mixtures

The highly exothermic reaction between arsenic trifluoride and sulphur trioxide was carried out in an one-necked round bottom flask which was fitted with a long water-cooled condenser. The top of the condenser was fitted with a dropping-funnel which carried a drying tube, containing either magnesium perchlorate or phosphorus pentoxide. For mixtures in which sulphur trioxide was in excess, arsenic trifluoride was added slowly through the dropping-funnel into a weighed amount of sulphur trioxide; and for mixtures in which arsenic trifluoride was in excess, sulphur trioxide was added to a weighed amount of arsenic trifluoride. A number of arsenic trifluoride-sulphur trioxide mixtures were thus prepared (Table 1), and each mixture was studied by F^{19} n.m.r. spectroscopy.

TABLE 1. AsF_3 - SO_3 MIXTURES

WEIGHT OF REACTANTS (g)		MOLE RATIO OF MIXTURE
AsF_3	SO_3	AsF_3 : SO_3
78.6	23.1	1 : 0.485
68.81	29.78	1 : 0.714
50.0	23.0	1 : 0.763
117.6	71.5	1 : 1.01
108.7	99.8	1 : 1.52
148.5	149.5	1 : 1.66
34.4	41.9	1 : 2.01
84.8	126.7	1 : 2.46
40.1	69.8	1 : 2.88
28.7	69.0	1 : 3.96
11.2	32.9	1 : 4.85
9.1	3 2.9	1 : 5.96

(iii) Nuclear Magnetic Resonance Spectroscopy

F^{19} nuclear magnetic resonance spectra in this work were obtained with a Varian Associates H.R. 60 spectrometer operating at a field strength of 14,000 gauss and at an r.f. frequency of 56.4 Mc/sec. Intensity measurements were made with the aid of an electronic integrator. Chemical shifts were measured with respect to disulphuryl fluoride as an internal reference; they are measured in cycles/sec. (c/s), and they are also expressed as a unitless quantity in parts per million (ppm) by using the equation $(\nu' - \nu)/\nu$ where $(\nu' - \nu)$ represents the chemical shift in c/s and ν the fixed r.f. frequency.

The theory of the nuclear magnetic resonance technique may be briefly described as follows (9). The F^{19} nucleus possesses a nuclear spin angular momentum, $I = \frac{1}{2}$ in $h/2\pi$ units, which gives rise to a nuclear magnetic moment, $\mu = \gamma (Ih/2\pi)$ where γ is the magnetogyric ratio of the F^{19} nucleus and h is Planck's constant. In the experiment, the sample is subject to the simultaneous action of a strong external magnetic field and an r.f. frequency, directed at right-angles to each other and at right-angles to the axis of the sample. The F^{19} nuclei in the sample may take up 2I+1 distinct orientations about the direction of the magnetic field Ho, and these orientations correspond to 2I+1 quantised energy levels with values

$$-\mu Ho, \; -\frac{I-1}{I}\mu Ho, \; \ldots\ldots\ldots \; +\frac{I-1}{I}\mu Ho, \; +\mu Ho.$$

These levels are equally spaced, the separation between them being $\mu Ho/I$. For the F^{19} nucleus, $I = \frac{1}{2}$, there are only two energy levels, namely $E = -\mu Ho$ and $E = +\mu Ho$, and the separation between them is $2\mu Ho$. At resonance, the F^{19} nuclei absorb this amount of energy from the applied r.f. field and undergo a transition from the lower energy level to the upper energy level. This absorption of energy gives rise to the nuclear magnetic resonance spectrum. The conditions for absorption by a nucleus are modified by the local magnetic field at the nucleus. This local magnetic field is determined by a number of factors including the polarization of remote parts of the sample, magnetic moments (nuclear or electronic) of neighbouring molecules, and intramolecular effects due to other nuclei and electrons in the same molecule. Hence, nuclei in different chemical environment will give resonance signals at different frequencies, and the intensity of each signal is proportional to the number of nuclei in each particular chemical environment in the molecule. Each signal is characterized by measuring its chemical shift, that is, its relative position with respect to the signal of an internal, or external, reference. (An internal reference is a compound which is dissolved in, but chemically inert to, the sample. An external reference is a compound which is enclosed in a separate compartment in the sample tube; in this work, the reference compound was sealed in a small thin capillary tube which was then supported in the centre of the main sample tube.)

Nuclear spins of neighbouring non-equivalent nuclei, usually separated by one, two or three chemical bonds, will interact, or couple, with one another via the electrons of the bonds, and the signals in the spectrum at high resolution show fine-structures as a result. Take, for instance, the simplest case of two non-equivalent nuclei, with $I = \frac{1}{2}$, bonded by a covalent bond, e.g. HF. As a result of spin-spin interaction, both the H^1 and F^{19} signals are split into doublets. The splitting, in cycles/sec., is a measure of the coupling constant J which is independent of temperature and the applied magnetic field.

More complicated multiplet patterns are obtained in cases where a set of two or more equivalent nuclei interacts with a set of two or more different equivalent nuclei and also for cases where I is greater than $\frac{1}{2}$.

The n.m.r. spectrum may be modified also if the molecules being measured are taking part in various rate processes. An example of such a process is the phenomenon of exchange of nuclei between different chemical positions. Take, for instance, the exchange taking place between two chemical positions, e.g., in a mixture of water and alcohol, the proton-exchange between water molecules (site A) and the hydroxyl position in the alcohol (site B). If there is no exchange the proton spectrum will consist of two separate signals at frequencies ω_A and ω_B, (neglecting any spin-spin coupling effects); if the exchange is slow, the proton spectrum will still consist of two signals, somewhat broadened and closer to each other; but if the exchange is rapid, these two signals will collapse into one. This resulting resonance signal will centre on a mean frequency, ω_{mean}, given by the equation $\omega_{mean} = p_A \omega_A + p_B \omega_B$ where p_A and p_B represent the fraction population of nuclei at site A and site B respectively. When the population of nuclei on the two sites are equal, the resulting signal will be situated exactly midway between ω_A and ω_B; when there is an unequal population on the two sites, the resulting signal will be found closer to the frequency for the site which has the higher fractional population. Similar modification of the spectrum also occurs when the exchange of nuclei is taking place between more than two chemical positions.

(iv) Distillation of AsF_3 - SO_3 Mixtures

Distillations were carried out on the AsF_3-SO_3 mixtures having the mole ratios 1:1.01, 1:1.52, 1:2.01, 1:2.46, 1:2.88 and 1:3.96. Of these mixtures, the 1:1.01 and 1:2.01 mixtures were distilled under reduced pressures; and the 1:1.52, 1:2.88 and 1:3.96 mixtures were distilled under atmospheric pressure. Ordinary distilling apparatus was used. The boiling point of the distillate from each distillation is recorded in Table 4, and the F^{19} n.m.r. spectrum of each sample was studied.

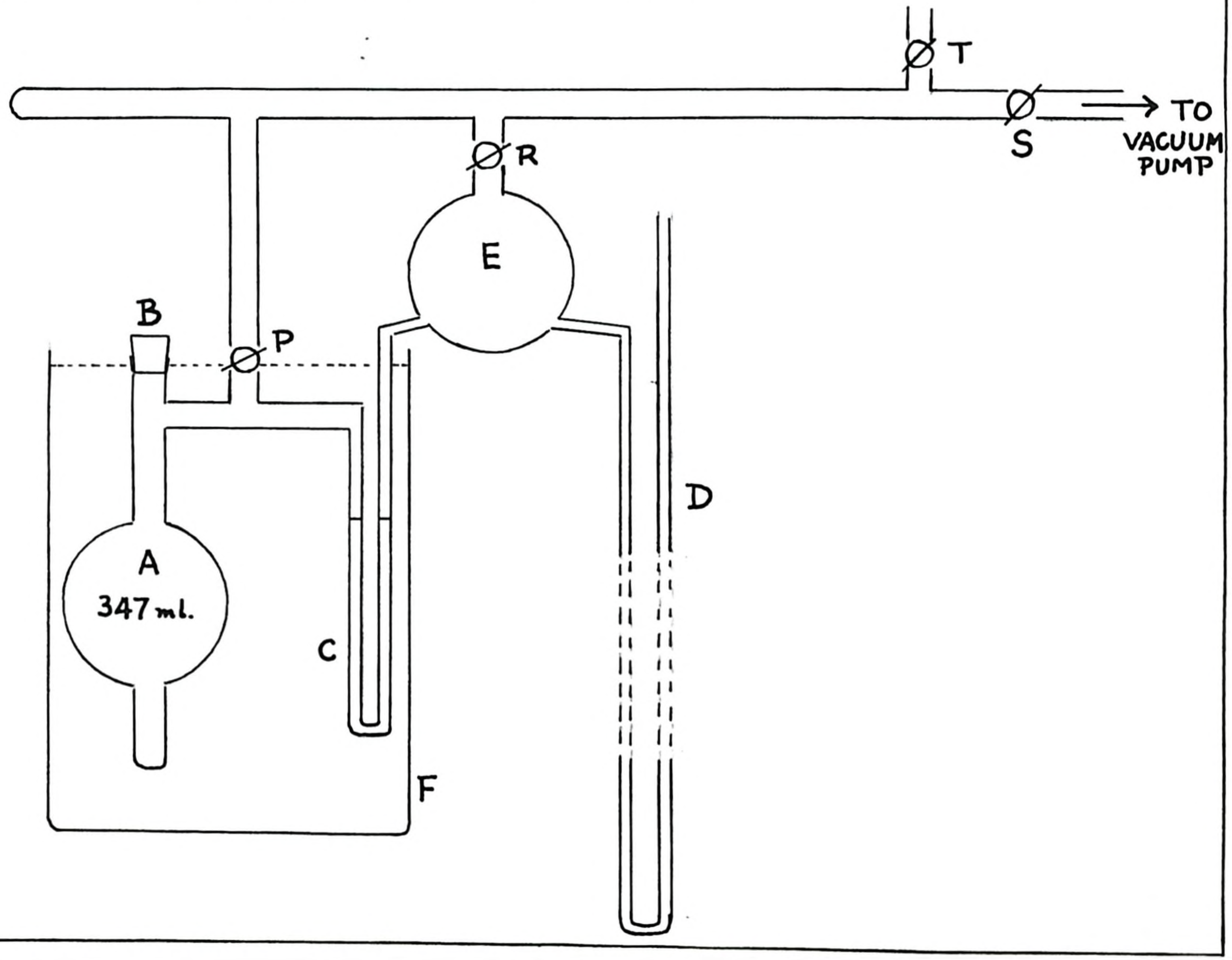
The 1:2.46 mixture was fractionally distilled under atmospheric pressure, using a conventional fractionating column. Fractions of distillate were collected at boiling points which appeared to remain steady or over a convenient boiling range. Each fraction was then examined by F^{19} n.m.r. spectroscopy.

(v) Vapour-density Measurements

Vapour-density measurements were made on various samples of the distillate in order to determine its molecular weight. The measurements were made with the aid of the apparatus shown in Figure 2. It consisted of a vessel A which was connected to a U-tube C through a side-arm. The U-tube contained Fluorolube oil, Grade HO-125 (Hooker Chemical Corporation) which was found to be chemically resistent to the vapour of the AsF_3-SO_3 mixtures. D is a mercury manometer and E an air chamber which served to regulate the movement of the oil and mercury. The vessel A, the side-arm and the U-tube were placed in the temperature-bath F.

In the experiment, a weighed amount of the sample was introduced by means of a dropping-funnel into the bottom of vessel A through the opening B which was afterwards closed with a stopper. With stopcock T closed, but stopcocks P, R and S opened, the whole system was evacuated while the sample was kept at liquid-nitrogen temperature. After evacuating the system, stopcocks P, R and S were closed, liquid nitrogen removed and the whole of vessel A and the U-tube were placed in the temperature-bath to vapourize the sample. As the sample was being vapourized, a pressure was generated inside the vessel A which registered on the U-tube oil manometer. Dry air was then let in through the stopcocks T and R to maintain the levels in the two arms of the U-tube at the same height. Thus, a pressure equivalent to that inside the vessel A was registered on the mercury manometer D. The molecular weight of the sample was then calculated from these values of temperature and pressure by making use of the ideal gas equation. The volume of the vessel A and the side-arm was measured by measuring the pressure of completely vaporized samples of weighed amounts of chloroform and carbon tetrachloride.

FIGURE 2 VAPOUR-DENSITY APPARATUS



(vi) Chemical Analysis

Three samples of the distillate were chemically analysed for fluorine and sulphur. One sample was obtained by the distillation of the 1:1.01 mixture under reduced pressure; another one was obtained by the fractional distillation of the 1:2.46 mixture under atmospheric pressure; and the third sample was obtained from the distillation of the 1:3.96 mixture under atmospheric pressure. Sulphur was determined by precipitation of sulphate as barium sulphate in the usual manner after first hydrolysing the sample. The method of Willard and Winter (10) was used for the fluorine analysis. The sample was first decomposed by heating with 60% perchloric acid to give a mixture of hydrofluoric acid and fluorosilicic acid which was distilled at a temperature below 135°C. from the resulting solution and condensed. The fluoride in the distillate was determined as lead chlorofluoride.

CHAPTER III ARSENIC TRIFLUORIDE - SULPHUR TRIOXIDE MIXTURES

(i) Possible Reactions and Products

A vigorous, exothermic reaction occurs when sulphur trioxide is added to arsenic trifluoride. It has been mentioned in Chapter I that this reaction did not proceed to the formation of disulphuryl fluoride and oxysulphate. The most probable route for this reaction to follow, then, is that taken by most fluorides of the Group V elements and the alkaline earth metals - namely the production of fluorosulphates. On the addition of sulphur trioxide to arsenic trifluoride, the first product, therefore, would be expected to be $AsF_2(SO_3F)$. If the reaction is complete and quantitative, the formation of $AsF(SO_3F)_2$ would follow only when the mole ratio of $AsF_3:SO_3$ exceeds 1:1, and no $As(SO_3F)_3$ would be formed until the mole ratio exceeds 1:2; thus

[4] $AsF3 + SO_3 \xrightarrow{\hspace{3em}} AsF_2(SO_3F)$

[5] $AsF_3 + 2SO_3 \xrightarrow{\hspace{3em}} AsF(SO_3F)_2$

[6] $AsF_3 + 3SO_3 \xrightarrow{\hspace{3em}} As(SO_3F)_3.$

So that, when the mole ratio of $AsF_3:SO_3$ is less than 1:1, some arsenic trifluoride will remain unreacted; between 1:1 and 1:2, $AsF(SO_3F)_2$ will be expected to coexist with $AsF_2(SO_3F)$; and between 1:2 and 1:3, $As(SO_3F)_3$ will be expected to coexist with $AsF(SO_3F)_2$.

(ii) AsF_3-SO_3 Mixtures with Mole Ratios less than 1:1

Two mixtures with mole ratios 1:0.435 and 1:0.763 were studied. It was expected that in these mixtures some arsenic trifluoride would remain unreacted. Two F^{19} n.m.r. peaks would be expected in the region characteristic of fluorine-on-arsenic (As-F region) and one peak in the region characteristic of fluorine-on-sulphur (S-F region). The spectrum, at room temperature however, showed only two peaks. In the case of the 1:0.763 mixture, for example, these peaks appeared at +137 c/s and $+5.15 \times 10^3$ c/s, using disulphuryl fluoride as the internal reference (Figure 3). An external reference of arsenic trifluoride gave a signal at 135 c/s to low field of the peak at $+5.15 \times 10^3$ c/s. Gutowsky and Hoffman (11) have previously measured the chemical shifts of sulphur hexafluoride and arsenic trifluoride, using fluorine gas at 25 atmospheres as the reference compound, and obtained the following results:

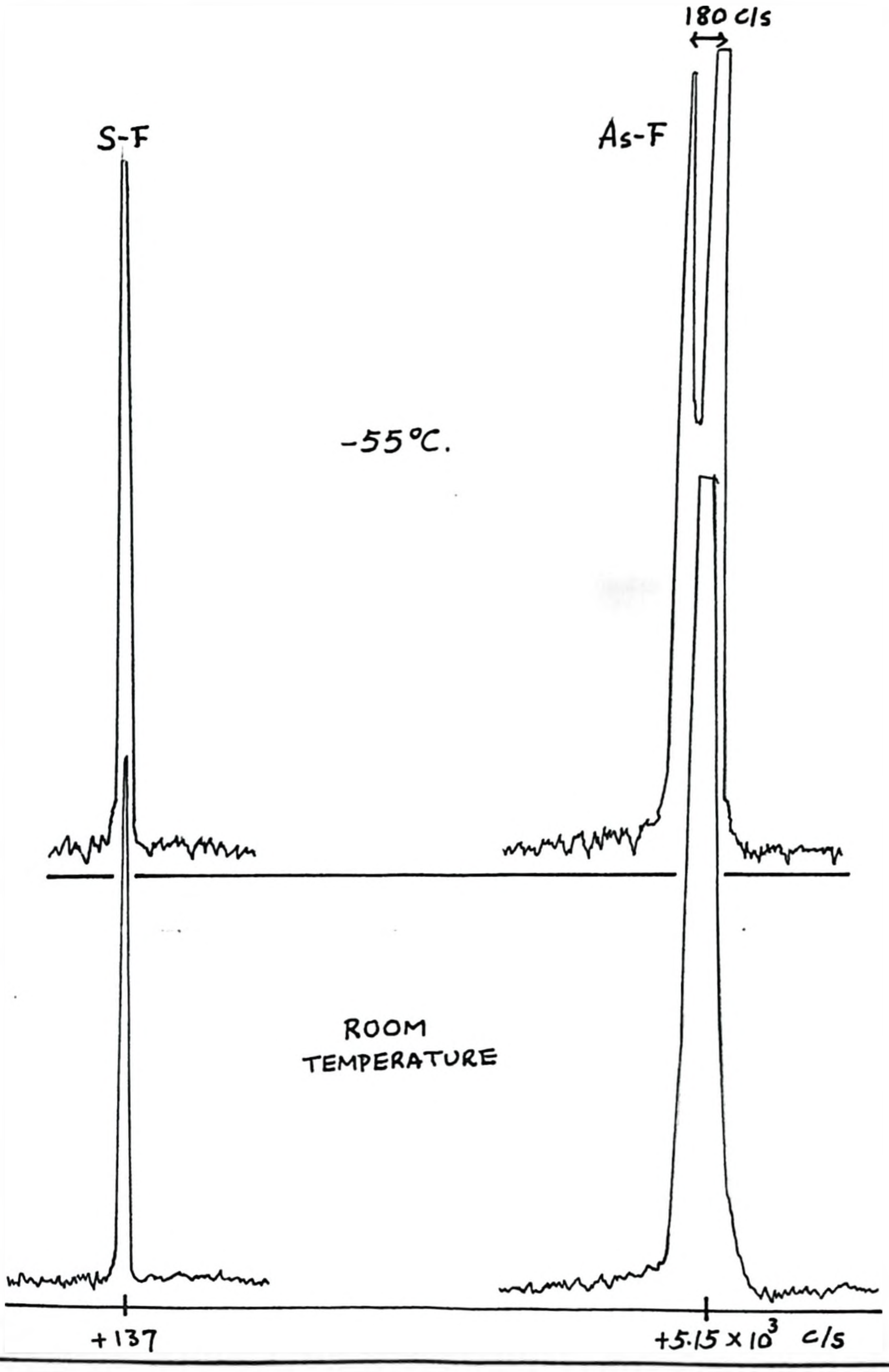
Compound	SF_6	AsF_3
Chemical Shift	375.6 ppm	469.1 ppm

In order to identify the two signals in our spectra, the chemical shifts were converted to values in ppm with respect to fluorine gas. (The conversion was done by relating the chemical shift of antimony pentafluoride from disulphuryl fluoride (12) to the chemical shift of antimony pentafluoride from fluorine gas (11) so that the chemical shift of disulphuryl fluoride from fluorine gas could be calculated. This value of chemical shift of disulphuryl fluoride was then added to the chemical shifts of the signals in our spectra to obtain corresponding chemical shifts with respect to fluorine gas. Rothenbury (12) found that the spectrum of antimony pentafluoride consists of three signals while Gutowsky and Hoffman reported only one value of chemical shift for antimony pentafluoride without specifying which signal was being referred to. Hence the results of the conversion might involve an error of ± 18 ppm.) The chemical shift +137 c/s became approximately 410 ppm, and $+5.15\text{x}10^3$ c/s became 485 ppm, while the chemical shift of the arsenic trifluoride signal (external reference) was 461 ppm. Thus, the peak at $+5.15\text{x}10^3$ c/s can be attributed to As-F fluoride atoms, while the peak at +137 c/s can be attributed to S-F fluorine atoms.

The spectra of these two mixtures were also observed at low temperatures. With decreasing temperature, the As-F peak broadened. For the 1:0.485 mixture, at -27°C., the peak width (at half-height) of the As-F peak increased to 30 c/s from about 20 c/s at room temperature; then at -55°C., the width became 114 c/s, while the width of the S-F peak remained unchanged throughout (5.1 c/s at room temperature, 5.2 c/s at -55°C.). In the case of the 1:0.763 mixture, at -55°C., the As-F peak split into two with a separation of 180 c/s, (Figure 3). By comparing with the signal of arsenic trifluoride (External reference), the lower field peak which is only 45 c/s from the arsenic trifluoride external reference peak can be assigned to unreacted arsenic trifluoride while the higher field peak is attributed to another type of As-F fluorine atoms presumably as $-OAsF_2$ groups in the new compound $AsF_2(SO_3F)$. The relative intensities of these two As-F peaks were $AsF_3/-OAsF_2 = 1/2.23 \pm 0.11$. Again, the width of the S-F peak remained unchanged at 6 c/s.

The constant width of the S-F peak with respect to temperature is an indication of the existence of only one type of S-F fluorine bond in the mixture and this presumably indicates the presence of a single type of $-SO_3F$ group. The merging of the two As-F peaks at room temperature indicates rapid fluorine-exchange between arsenic trifluoride and $AsF_2(SO_3F)$, the rate of which can be greatly reduced by lowering the temperature. At -55°C., the exchange is sufficiently slow that two peaks were observed. The fact that the As-F peak for the 1:0.435 mixture did not split even at -55°C. is probably due to the higher concentration of unreacted arsenic trifluoride increasing the rate of fluorine-exchange. The temperature of -55°C. was the lowest that could be used for observing the n.m.r. signals for these

FIGURE 3 F^{19} N.M.R. SPECTRUM OF AsF_3-SO_3 MIXTURE OF MOLE RATIO 1:0.763 CHEMICAL SHIFTS FROM $S_2O_5F_2$ (INTERNAL) AT 56.4 Mc/s



mixtures. The mixture became highly viscous at such low temperatures and the signals began to broaden and diminish and eventually disappeared at temperatures below -65°C.

The relative intensities of the n.m.r. peaks in the spectrum can be utilized to deduce the composition of the mixtures in terms of relative amounts of arsenic trifluoride and $AsF_2(SO_3F)$. For example, the relative intensities of the n.m.r. peaks of the 1:0.763 mixture were $S{-}F/AsF_3/{-}OAsF_2 = 1/0.84 \pm 0.01/2.10 \pm 0.11$. Since in $AsF_2(SO_3F)$ there is only one $-SO_3F$ group but two fluorine atoms bonded to arsenic, one mole of $AsF_2(SO_3F)$ will give n.m.r. signals in relative intensities $S{-}F/{-}OAsF_2 = 1/2$; and since there are three fluorine atoms in one molecule of arsenic trifluoride, one mole of AsF_3 will give an n.m.r. signal of relative intensity 3. But in the spectrum the relative intensity of the AsF_3 peak was 0.84 ± 0.01; this may be accounted for by 0.28 mole of AsF_3. Hence the composition of this mixture is found to be 1 $AsF_2(SO_3F)$:0.28 AsF_3. Expressed in mole%, the composition is 78.1% $AsF_2(SO_3F)$:21.9% AsF_3. From the mole ratio of this mixture, $AsF_3:SO_3 = 1:0.763$, assuming that the reaction according to Equation 4 is complete and quantitative, the relative amounts of the expected products are 0.763 $AsF_2(SO_3F)$ and 0.237 AsF_3, or 76.3% $AsF_2(SO_3F)$ and 23.7% AsF_3. Comparison can be made in another way. The composition of this mixture can be formulated as $AsF_3{:}xSO_3$, and then compared with the mole ratio of the mixture. The n.m.r. results give the composition AsF_3:0.781 SO_3, while the composition calculated from the weights of arsenic trifluoride and sulphur trioxide used to make up the mixture is 1:0.763. Both methods of comparison yield good agreement. These values are listed in Table 2.

In the case of the 1:0.485 mixture, the relative amounts of the expected products are 0.485 $AsF_2(SO_3F)$ and 0.515 AsF_3, or 48.5% $AsF_2(SO_3F)$ and 51.5% AsF_3. One mole of $AsF_2(SO_3F)$ would be expected to give relative intensities S-F/As-F = 1/2. The relative intensities of the two peaks were however found to be S-F/As-F = 1/5.40 ± 0.06. This can be accounted for by assuming the presence of 1.13 moles of unreacted arsenic trifluoride. This composition can be expressed as 46.9% $AsF_2(SO_3F)$ and 53.1% AsF_3, and can be formulated as AsF_3:0.469 SO_3 (Table 2). Comparing the composition obtained from n.m.r. data with the composition calculated from the weights of arsenic trifluoride and sulphur trioxide used to make up the mixture, as for the previous 1:0.763 mixture, it may be seen in Table 2 that good agreement is obtained.

TABLE 2 AsF_3-SO_3 MIXTURES

AsF_3:SO_3 Mole Ratio	Expected Products		Relative Intensities of n.m.r. Peaks*				Composition of Mixture From Relative Intensities of n.m.r. Peaks	
	Relative Moles	Mole %	S-F	AsF_3	$OAsF_2$	OAsFO	Mole %	AsF_3:xSO_3
1:0.485	0.515 AsF_3 0.485 $AsF_2(SO_3F)$	51.5 48.5	1	5.40±0.06			52.4 AsF_3 47.6 $AsF_2(SO_3F)$	1:0.48
1:0.763	0.237 AsF_3 0.763 $AsF_2(SO_3F)$	23.7 76.3	1	0.84 ±0.01	2.10 ±0.11		21.9 AsF_3 78.1 $AsF_2(SO_3F)$	1:0.78
1:1.01	0.99 $AsF_2(SO_3F)$ 0.01 $AsF(SO_3F)_2$	99 1	1	0.13 ±0.03	1.77 ±0.05	0.10 ±0.02	4 AsF_3 88 $AsF_2(SO_3F)$ 8 $AsF(SO_3F)_2$	1:1.04
1:1.52	0.48 $AsF_2(SO_3F)$ 0.52 $AsF(SO_3F)_2$	48 52	4.17 ±0.21		3.56 ±0.02	1	61.1 $AsF_2(SO_3F)$ 34.2 $AsF(SO_3F)_2$ 4.7 $As(SO_3F)_3$	1:1.44
After Refluxing			2.91 ±0.04		1.82 ±0.03	1	47.6 $AsF_2(SO_3F)$ 52.4 $AsF(SO_3F)_2$	1:1.51

TABLE 2 (Cont'd) AsF_3-SO_3 MIXTURES

AsF_3:SO_3 Mole Ratio	Expected Products		Relative Intensities of n.m.r. Peaks*				Composition of Mixture From Relative Intensities of n.m.r. Peaks	
	Relative Moles	Mole %	S-F	AsF_3	$OAsF_2$	OAsFO	Mole %	AsF_3:xSO_3
1:2.01	0.99 $AsF(SO_3F)_2$ 0.01 $As(SO_3F)_3$	99 1	3.17 ±0.05		2.07 ±0.04	1	49.8 $AsF_2(SO_3F)$ 47.8 $AsF(SO_3F)_2$ 2.4 $As(SO_3F)_3$	1:1.54
1:2.46	0.54 $AsF(SO_3F)_2$ 0.46 $As(SO_3F)_3$	54 46	2.57 ±0.05		0.36 ±0.01	1	13.7 $AsF_2(SO_3F)$ 76.3 $AsF(SO_3F)_2$ 9.9 $As(SO_3F)_3$	1:1.96
1:2.88	0.12 $AsF(SO_3F)_2$ 0.88 $As(SO_3F)_3$	12 88	6.91 ±0.30			1	37.4 $AsF(SO_3F)_2$ 62.5 $As(SO_3F)_3$	1:2.63
1:3.96	1 $As(SO_3F)_3$	100	13.8 ±0.4			1	20.3 $AsF(SO_3F)_2$ 79.7 $As(SO_3F)_3$	1:2.80

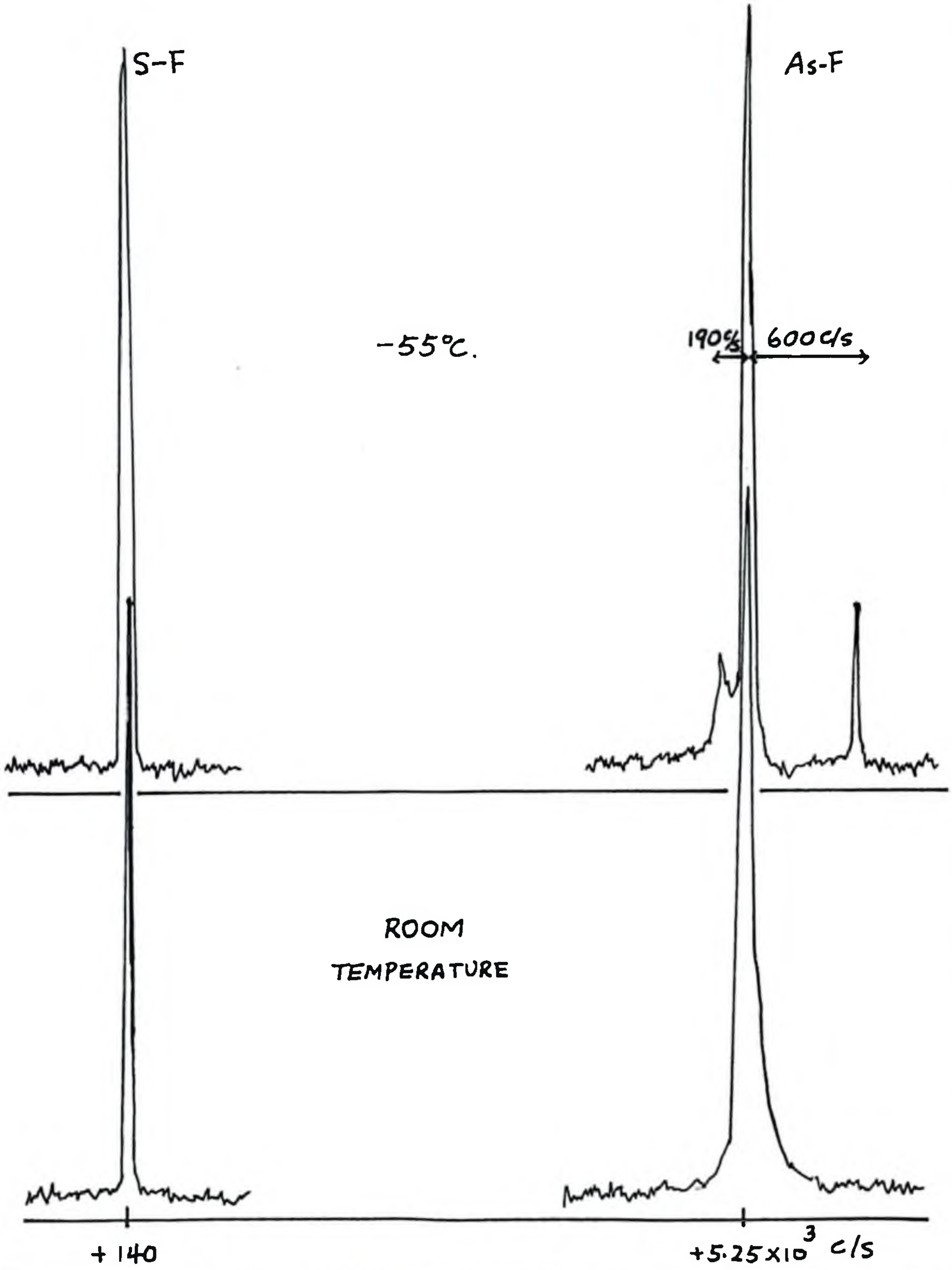
* Values of relative intensities of the n.m.r. peaks in the spectrum for each mixture as listed in this table are the mean values of four or five measurements of the same spectrum.

(iii) AsF_3-SO_3 Mixture of Mole Ratio 1:1.01

If the reaction according to Equation 4 is complete the mixture should consist entirely of $AsF_2(SO_3F)$. The n.m.r. spectrum at room temperature indeed showed one S-F peak and one As-F peak with relative intensities S-F/As-F = 0.50±0.01 (Figure 4 and Table 2), in agreement with the production of $AsF_2(SO_3F)$. But at -55°C., the S-F peak broadened from 7 c/s to 12.5 c/s, while in the As-F region two small additional peaks appeared. One of these two peaks appeared at lower field by 190 c/s and is assigned, as in the previous section, to unreacted arsenic trifluoride. The other peak, appearing at higher field by 600 c/s, is assigned to the compound $AsF(SO_3F)_2$ for reasons which will be clear in the next section. The intensities of these two peaks were very low: the AsF_3 peak having about 1/15 of the intensity of the main $AsF_2(SO_3F)$ peak, while the $AsF(SO_3F)_2$ peak had about 1/20 of the intensity of the main peak. The broadening of the S-F peak also indicates that this signal is not due to one type of S-F fluorine atoms alone.

That all three species, AsF_3, $AsF_2(SO_3F)$ and $AsF(SO_3F)_2$ are observed can only mean that the reactions described by Equations 4 and 5 are not complete; $AsF(SO_3F)_2$ must begin to form before all of the arsenic trifluoride

FIGURE 4 F^{19} N.M.R. SPECTRA OF AsF_3-SO_3 MIXTURE OF MOLE RATIO 1:1.01
CHEMICAL SHIFTS FROM $S_2O_5F_2$ (INTERNAL) AT 56.4 Mc/s



is converted to $AsF_2(SO_3F)$. Since at room temperature only one As-F peak was observed, fluorine-exchange must be occuring between all three species.

Because the intensities of the small peaks could not be measured accurately, only approximate values of relative intensities of the peaks and for the relative amounts of the components are given in Table 2.

(iv) AsF_3-SO_3 Mixture of Mole Ratio 1:1.52

In this mixture, $AsF_2(SO_3F)$ and $AsF(SO_3F)_2$ would be expected to be produced in very nearly equal amounts if reaction of the sulphur trioxide was complete. There are, therefore, two types of fluorine-on-sulphur and two types of fluorine-on-arsenic atoms, and the n.m.r. spectrum would be expected to show four signals. The spectrum, at room temperature, showed two peaks in the As-F region, but only one in the S-F region (Figure 5). The As-F peak which appeared at higher field than the $-OAsF_2$ peak by about 540 c/s is assigned to -OAsFO- groups in $AsF(SO_3F)_2$. At -55°C., there was no apparent change in the spectrum except that the peak width of the S-F peak increased to 35.6 c/s from 7 c/s at room temperature. This is consistent with the idea that there are two types of fluorine-on-sulphur atoms undergoing rapid exchange between each other, presumably by exchange of fluorosulphate groups. The two As-F peaks overlapped to a small extent. The reason for this overlap is probably that there is slow fluorine-exchange occuring between $AsF_2(SO_3F)$ and $AsF(SO_3F)_2$, and possibly a very small amount of unreacted arsenic trifluoride.

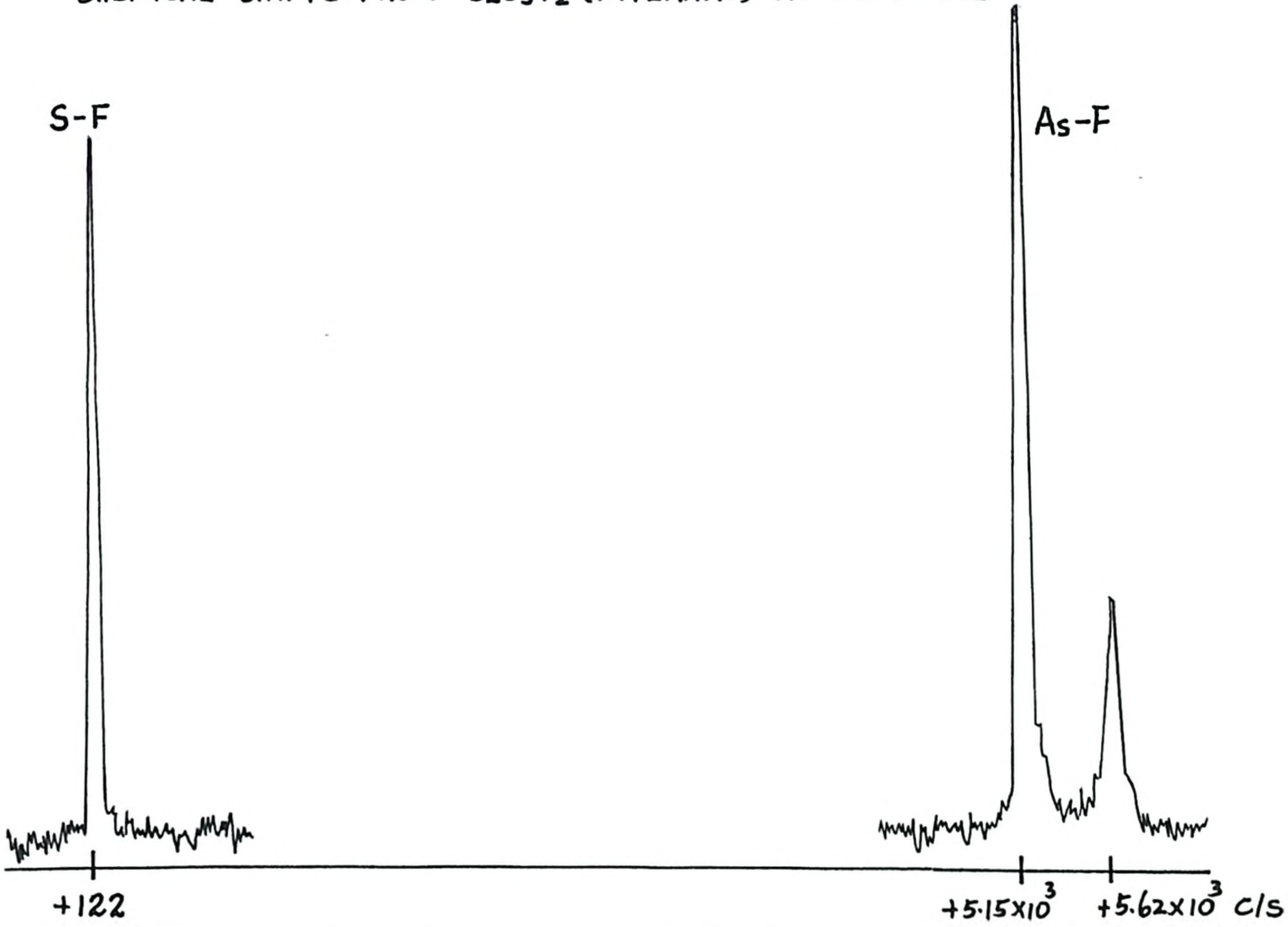
Assuming that the reactions according to Equations 4 and 5 are complete and quantitative, the relative amounts of the expected products in this mixture are 0.48 $AsF_2(SO_3F)$

and 0.52 $AsF(SO_3F)_2$, or expressed as mole %, 48% $AsF_2(SO_3F)$ and 52% $AsF(SO_3F)_2$. The relative intensities of the n.m.r. peaks were S-F/$-OAsF_2$/-OAsFO = 4.17±0.21/3.56±0.02/1 (Table 2). Since there is only one fluorine atom in $AsF(SO_3F)_2$, one mole of this would account for the -OAsFO- peak; and since there are two fluorine atoms in $AsF_2(SO_3F)$, 1.78 moles of this would account for the relative intensity of the $-OAsF_2$ peak. These two compounds give a total relative intensity of 3.78 for the S-F peak. The difference from the value 4.17 ± 0.21 can be accounted for by 0.13 mole of $As(SO_3F)_3$. In order to make a comparison with the expected values, the composition is expressed as 61.1% $AsF_2(SO_3F)$, 34.2% $AsF(SO_3F)_2$ and 4.7% $As(SO_3F)_3$ (Table 2). This composition can also be formulated as AsF_3:1.44SO_3; the difference of this from the composition of the mixture as originally prepared by weight may be explained by the existence of a very small amount of unreacted sulphur trioxide.

The composition of this mixture was changed by refluxing the solution for two hours. The overlapping between the As-F peaks was greatly diminished and the intensity of the $AsF(SO_3F)_2$ peak grew somewhat at the expense of the $AsF_2(SO_3F)$ peak. The S-F peak at -55°C. increased in width to 58 c/s. The values of relative intensities of these peaks and the corresponding composition are recorded in Table 2.

FIGURE 5 F^{19} N.M.R. SPECTRUM OF AsF_3-SO_3 MIXTURE OF MOLE RATIO 1:1.52

CHEMICAL SHIFTS FROM $S_2O_5F_2$ (INTERNAL) AT 56.4 Mc/s



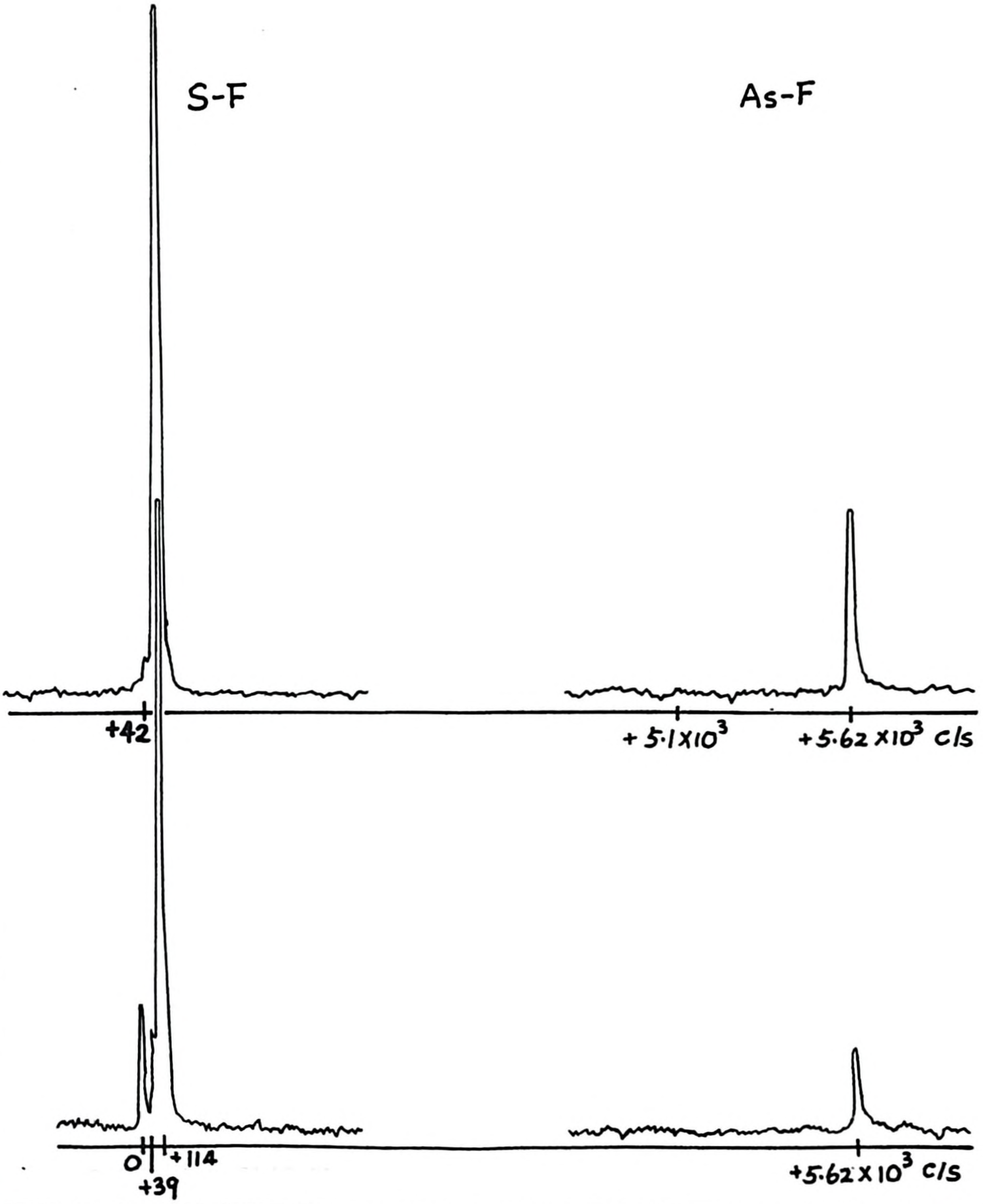
(v) AsF_3-SO_3 Mixture of Mole Ratio 1:2.01

If the reaction according to Equation 5 was complete this mixture should produce entirely $AsF(SO_3F)_2$. The spectrum showed the same three peaks as in the spectrum of the 1:1.52 mixture, indicating that the reaction is by no means complete. The relative intensities of the n.m.r. peaks for this mixture were S-F/-$OAsF_2$/-OAsFO = 3.17±0.05/2.07±0.04/1. These values and the corresponding composition for this mixture are listed in Table 2. The composition can be formulated as AsF_3,1.53SO_3 and the difference from the composition of the mixture as originally prepared by weight can be accounted for by the presence of some unreacted sulphur trioxide.

Raman spectra (13) lend support to this interpretation. For AsF_3-SO_3 mixtures with mole ratios from 1:0.5 to 1:1.5, spectral evidence has been obtained for the existence of unreacted arsenic trifluoride. For mixtures with higher mole ratios than this, there was no evidence for unreacted arsenic trifluoride, but evidence for unreacted sulphur trioxide was obtained.

FIGURE 6 F^{19} N.M.R. SPECTRA OF AsF_3-SO_3 MIXTURES WITH MOLE RATIOS 1:2.88 (TOP) AND 1:3.96 (BOTTOM)

CHEMICAL SHIFTS FROM $S_2O_5F_2$ (INTERNAL) AT 56.4 Mc/s



(vi) AsF_3-SO_3 Mixtures with Mole Ratios 1:2.88 and 1:3.96

At such high ratios of sulphur trioxide, $As(SO_3F)_3$ should be the main product (Equation 6). However, due to the incompleteness of the reaction, $AsF(SO_3F)_2$ is still an important product, as was shown by the n.m.r. spectra of these mixtures (Figure 6). Even the signal corresponding to $AsF_2(SO_3F)$ was just detectable in the spectrum of the 1:2.88 mixture, indicating the presence of very small amounts of this substance. In the S-F region, there was the usual, intense peak ascribed to $-SO_3F$ groups. In this region, for the 1:2.88 mixture, there was one additional small S-F peak at +42 c/s; for the 1:3.96 mixture, there were two additional small peaks, at +39 c/s and 0 c/s. The origin of the peaks at +39 c/s and +42 c/s is not understood. The peak at 0 c/s may be attributed to the presence of a very small amount of disulphuryl fluoride.

The relative intensities of the two main peaks in the spectrum were S-F/-OAsFO- = 6.91 ±0.30/1 for the 1:2.88 mixture, and S-F/-OAsFO- = 13.8 ± 0.4/1 for the 1:3.96 mixture (Table 2). These values give the 1:2.88 mixture the composition 37.4% $AsF(SO_3F)_2$ and 62.5% $As(SO_3F)_3$; and give the 1:3.96 mixture the composition 20.3% $AsF(SO_3F)_2$ and 79.7% $As(SO_3F)_3$. Since the corresponding compositions can be calculated to be AsF_3:2.63SO_3 and AsF_3:2.80SO_3 respectively, considerable amounts of unreacted sulphur trioxide were also present.

When the 1:2.88 mixture was distilled under atmospheric pressure, a liquid boiling at a constant temperature of 138°C. was obtained which had an n.m.r. spectrum identical with the supposed compound $2AsF_3.3SO_3$ obtained by the distillation of other mixtures. But before this temperature was reached, in the boiling range from room temperature to 135°C., a distillate was collected. The n.m.r. spectrum of this distillate, at high resolution, showed no As-F signals but a series of four S-F signals (Figure 7). These four S-F signals were identified (8) as follows:

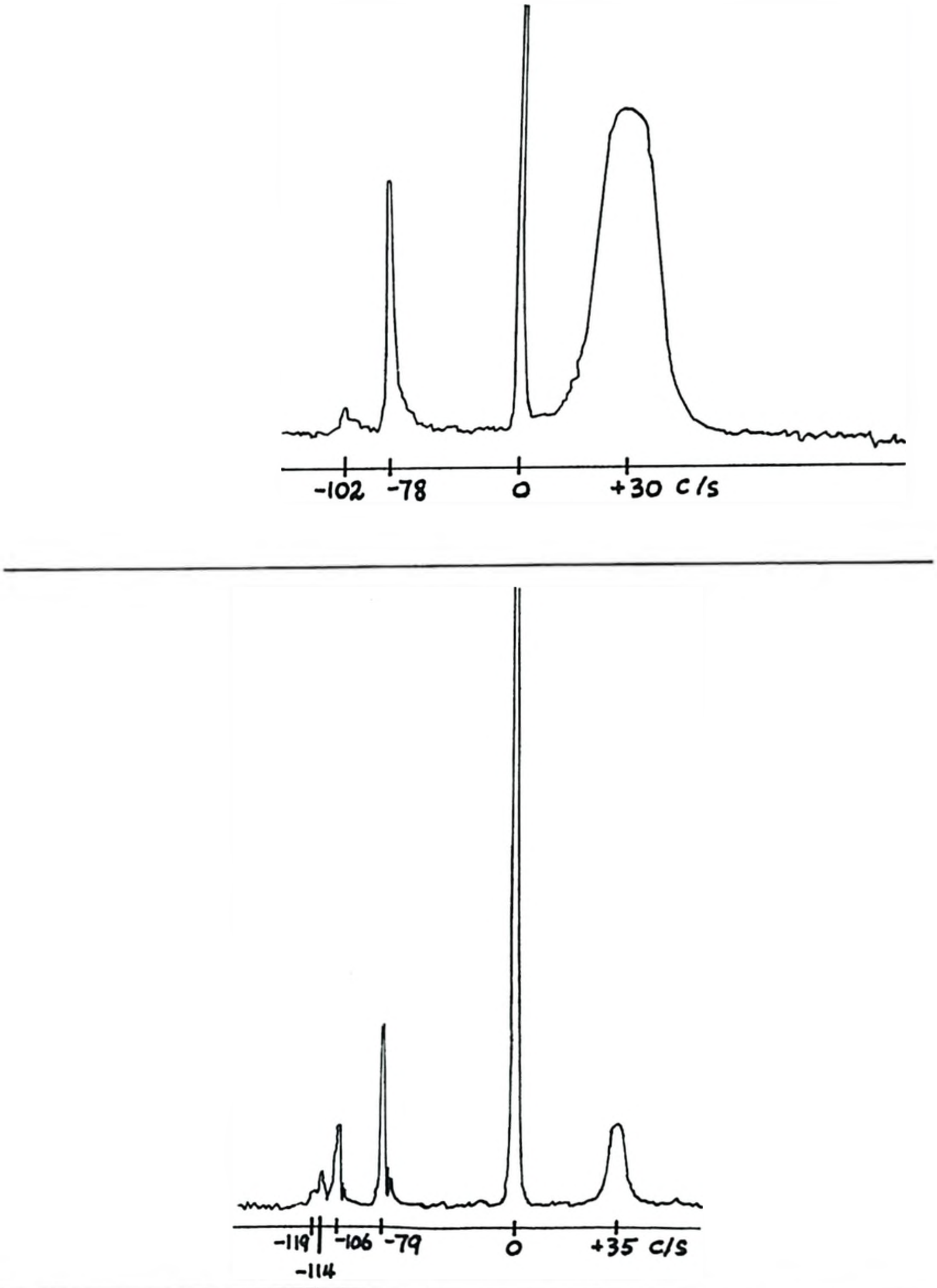
CHEMICAL SHIFTS*	-102	-78	0	+29.5
COMPOUND	$S_4O_{11}F_2$	$S_3O_8F_2$	$S_2O_5F_2$	$-S_2O_6F$

*Chemical shifts from $S_2O_5F_2$ (internal) in c/s at 56.4 Mc/s.

The assignment of the signal at +29.5 c/s to to $-S_2O_6F$ groups will be discussed in the next section.

The 1:3.96 mixture was similarly distilled. The n.m.r. spectrum of the distillate collected between room temperature and 95°C. showed a similar series of S-F peaks (Figure 7) which were assigned as follows:

FIGURE 7 F^{19} N.M.R. SPECTRA OF THE FIRST FRACTIONS OF DISTILLATE FROM 1:2·88 MIXTURE (TOP) AND 1:3·96 MIXTURE (BOTTOM)
CHEMICAL SHIFTS FROM $S_2O_5F_2$ (INTERNAL) AT 56·4 Mc/s



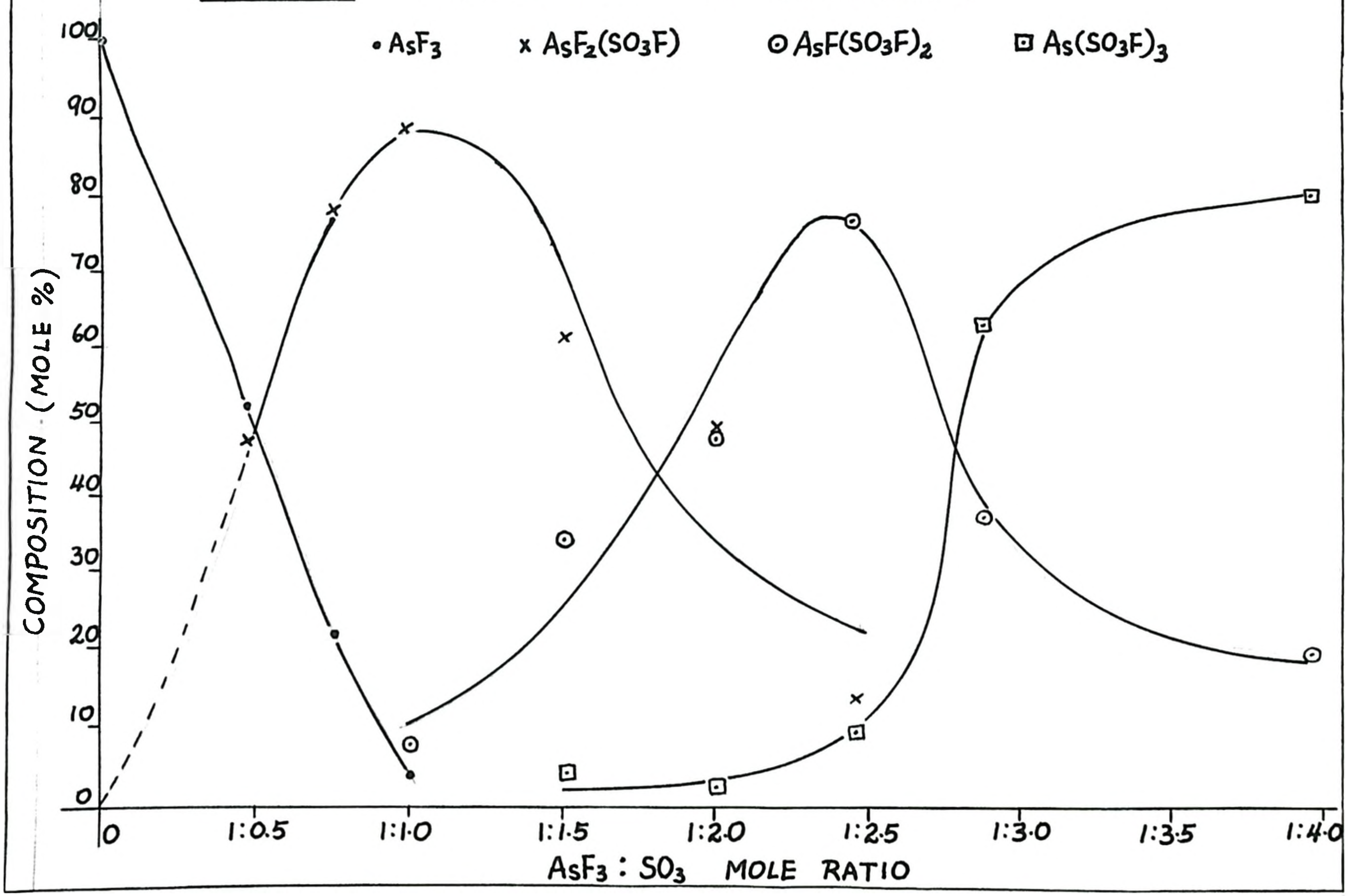
CHEMICAL SHIFTS*	-119	-114	-106	-79	0	+35
COMPOUND	$S_6O_{17}F_2$	$S_5O_{14}F_2$	$S_4O_{11}F_2$	$S_3O_8F_2$	$S_2O_5F_2$	$-S_2O_6F$

*Chemical shifts from $S_2O_5F_2$ (internal) in c/s at 56.4 Mc/s

No significant results were obtained from low-temperature measurements on the AsF_3-SO_3 mixtures with mole ratios 1:2.01, 1:2.88 and 1:3.96, nor on the mixtures with mole ratios 1:4.85 and 1:5.96 discussed in the next section, because these liquids became extremely viscous and the n.m.r. signals disappeared at temperature below -28°C. before any significant changes in the spectra were observed.

A plot of composition (mole %), obtained from n.m.r. results, for all these mixtures against AsF_3:SO_3 mole ratio is given in Figure 8.

FIGURE 8 COMPOSITION VS MOLE RATIO



(vii) AsF_3-SO_3 Mixtures with Mole Ratios 1:4.85 and 1:5.96

No As-F signals were observed in the F^{19} n.m.r. spectra of these two mixtures; we conclude that neither $AsF_2(SO_3F)$ nor $AsF(SO_3F)_2$ can exist in mixtures with such high concentration of sulphur trioxide. In the S-F region, more than one signal was observed.

For the 1:5.96 mixture, three S-F peaks were observed, (Figure 9) — one broad peak, and two sharp peaks about 100 c/s to low field from the broad peak. When disulphuryl fluoride, $S_2O_5F_2$, was added to serve as an internal reference, a sharp peak emerged from one side of the broad peak, and the chemical shifts for the three peaks were measured from this reference peak.

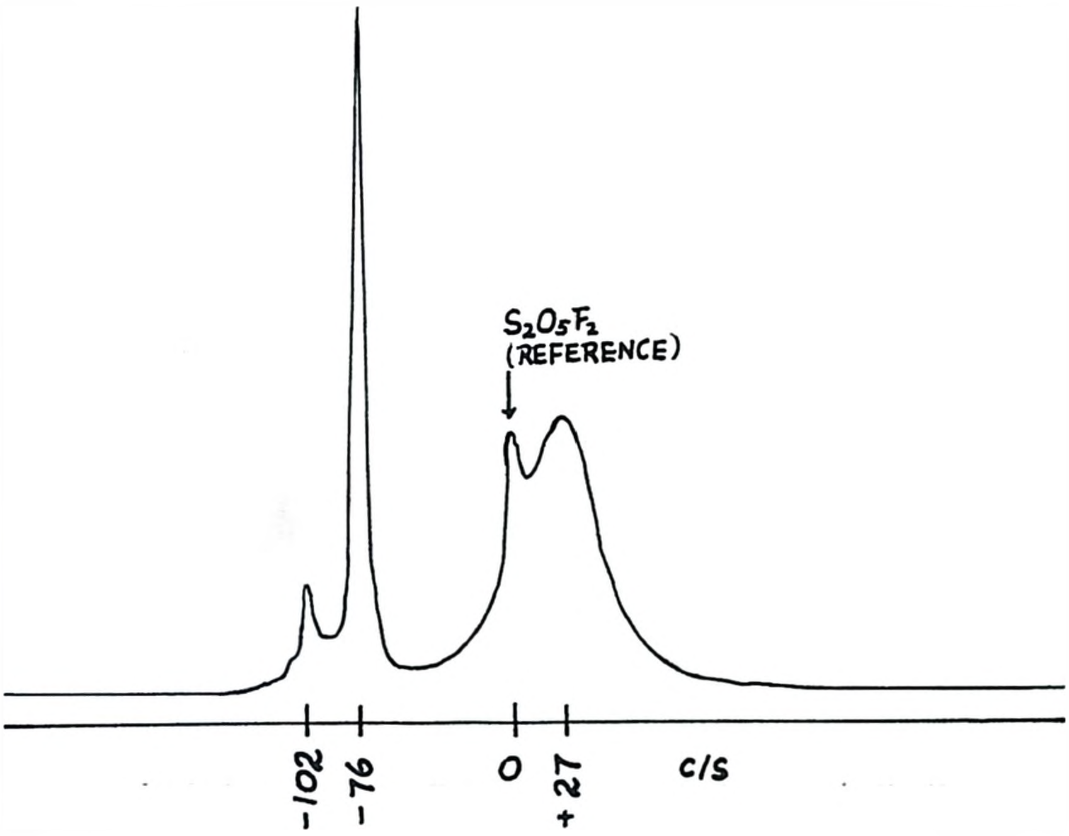
CHEMICAL SHIFTS*	-102	-76	+26.7
COMPOUND	$S_4O_{11}F_2$	$S_3O_8F_2$	$-S_2O_6F$

*Chemical shifts in c/s at 56.4 Mc/s

The two sharp peaks at lower field were identified as $S_3O_8F_2$ and $S_4O_{11}F_2$. At such high concentration of sulphur trioxide $As(SO_3F)_3$ is presumably the only fluorosulphate present. But in the presence of a large excess of sulphur trioxide it may be assumed that $-S_2O_6F$ groups would be formed in equilibrium with $As(SO_3F)_3$ and SO_3, that is,

FIGURE 9 F^{19} N.M.R. SPECTRUM OF AsF_3-SO_3 MIXTURE OF MOLE RATIO 1:5.96

CHEMICAL SHIFTS FROM $S_2O_5F_2$ (INTERAL) AT 56.4 Mc/s



$$-SO_3F + SO_3 \rightleftharpoons -S_2O_6F.$$

The broad peak at +26.7 c/s may be assigned to the $-S_2O_6F$ groups.

For the 1:4.85 mixture, there were two S-F peaks in the spectrum, 80 c/s apart. The peak at higher field was broad. When $S_2O_5F_2$ was added no new peak was observed, but the intensity of the broad peak grew somewhat. It is possible that the $S_2O_5F_2$ reference peak was concealed by the broad $-S_2O_6F$ peak. It may be argued further that in the 1:5.96 mixture disulphuryl fluoride was actually formed, though its n.m.r. signal was concealed by the $-S_2O_6F$ signal. In the 1:4.85 mixture, the peak at lower field by 80 c/s can be safely assigned to trisulphuryl fluoride, $S_3O_8F_2$.

The broad nature of the $-S_2O_6F$ peak makes it difficult to measure its chemical shift with accuracy. From the above mixtures, the chemical shift of this $-S_2O_6F$ peak from $S_2O_5F_2$ (internal) was found to be in the vicinity of +30 c/s; and this makes it possible to also assign the peaks of the first fractions of distillates from the 1:2.33 and 1:3.96 mixtures which appeared at +29.5 c/s and +35 c/s respectively to $-S_2O_6F$ groups.

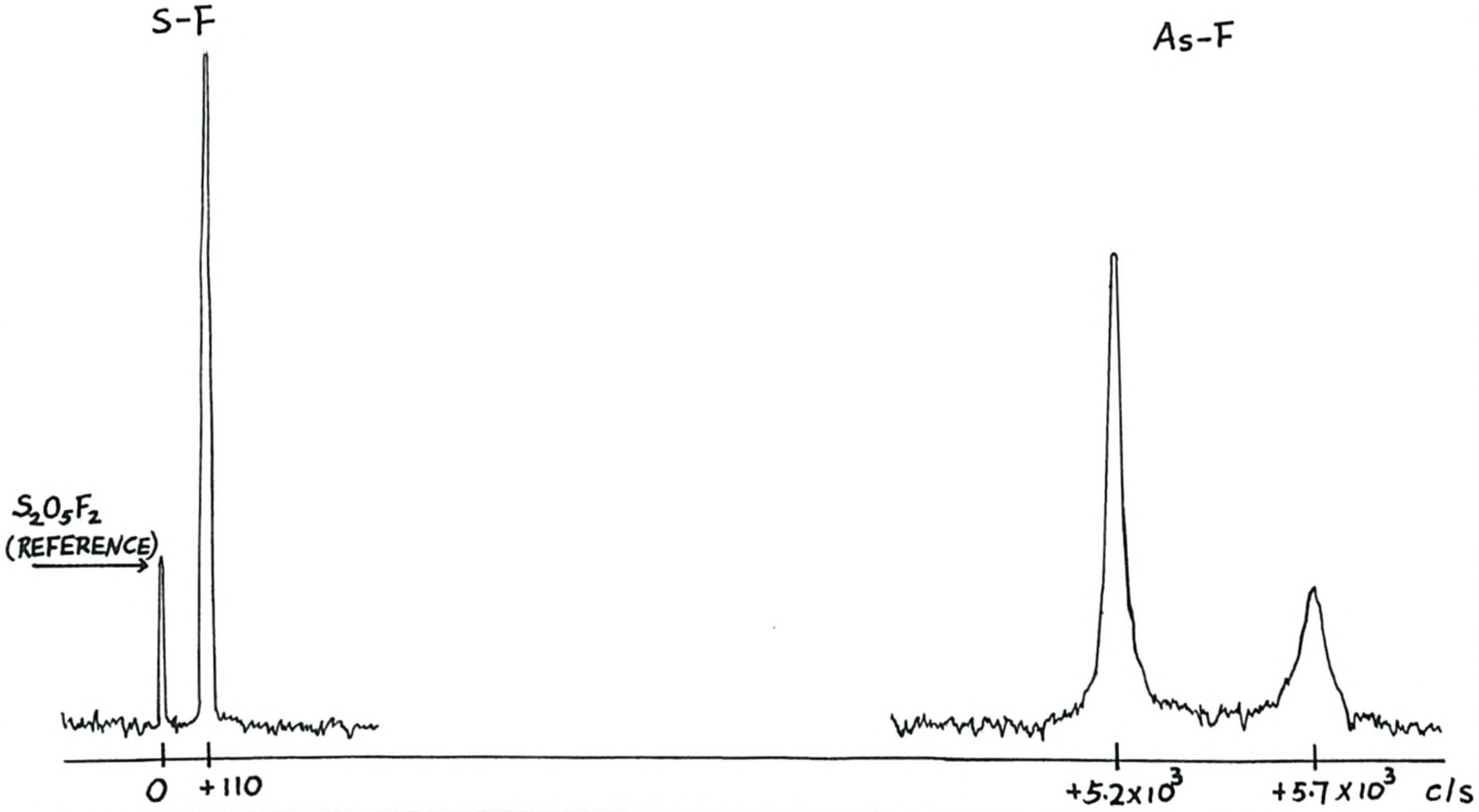
CHAPTER 1V $2AsF_3.3SO_3$ - A CONSTANT-BOILING MIXTURE

(i) Interpretation of the n.m.r. spectrum of $2AsF_3.3SO_3$

The information furnished by the n.m.r. spectra of arsenic trifluoride-sulphur trioxide mixtures can now be applied to the interpretation of the spectrum of the supposed compound $2AsF_3.3SO_3$. From each of the AsF_3-SO_3 mixtures discussed in Chapter 111, this liquid was obtained by distillation. When the distillation was carried out under atmospheric pressure, the boiling point of the liquid lay between 137.5°C. and 140°C.; when the distillation was carried out under reduced pressure, the boiling point was found to be 65.0°C./20 m.m. and 55.5°C./12 m.m. (Table 4). These various samples of the liquid showed similar F^{19} n.m.r. spectra, but the relative intensities of the peaks in each spectrum varied significantly from sample to sample. As mentioned in Chapter 1, the spectrum consists of three resonance peaks — one in the S-F region and two in the As-F region (Figure 10). Of the two peaks in the As-F region, the one at $+5.2x10^3$ c/s indicates the presence of $-OAsF_2$ groups, i.e., the compound $AsF_2(SO_3F)$; and the other peak at $+5.75x10^3$ c/s indicates the presence of -OAsFO- groups, i.e., the compound $AsF(SO_3F)_2$. The position of the single peak in the S-F region agrees with the presence of fluorosulphate groups. (Chemical shifts

FIGURE 10 F^{19} N.M.R. SPECTRUM OF $2AsF_3 \cdot 3SO_3$

CHEMICAL SHIFTS IN CYCLES/SEC. AT 56.4 Mc/s



of the n.m.r. peaks for each sample are listed in Table 3). This S-F peak broadens seven to eight times at a temperature of -55°C., and this is indicative of the presence of two or more fluorosulphate groups in different chemical environments. The As-F peaks are due to $AsF_2(SO_3F)$ and $AsF(SO_3F)_2$. If there was a strong interaction between them to form a complex, as Muetterties and Coffman suggested, they would have to exist always in equal amounts, and the relative intensities of the two As-F peaks would have to be exactly 2:1. On measuring the intensities of the peaks with the electronic integrator, it was found that this ratio is by no means always observed. The relative intensities of the three peaks come close to the ratio $S\text{-}F/\text{-}OAsF_2/\text{-}OAsFO\text{-} = 3/2/1$ only in some cases (Table 4), and the observed ratio depends on the pressure under which the distillation was carried out. The fact that these ratios vary from sample to sample can only mean that the distillate is not a definite compound but is probably better described as a constant-boiling mixture consisting principally of $AsF_2(SO_3F)$ and $AsF(SO_3F)_2$. In order to account for extra intensities in some of the S-F peaks, it must be assumed that small amounts of $As(SO_3F)_3$ can also be incorporated in the constant-boiling mixture.

Constant-boiling mixtures were obtained from the 1:1.01 and 1:2.01 AsF_3-SO_3 mixtures by distilling under reduced pressures. The boiling point was 55.5°C./12 m.m.

TABLE 3 N.M.R. SPECTRA OF CONSTANT-BOILING MIXTURES

CONSTANT-BOILING MIXTURE		CHEMICAL SHIFTS, C/S [*]		
SAMPLE NUMBER	FROM INITIAL AsF_3-SO_3 MIXTURE	S-F	$-OAsF_2$	-OAsFO-
1	1:1.01	+115	+5.2x10^{3}	+5.76x10^{3}
2	1:1.52	+122	+5.2x10^{3}	+5.75x10^{3}
3	1:2.01	+106	+5.2x10^{3}	+5.75x10^{3}
4	1:2.46	+109	+5.2x10^{3}	+5.75x10^{3}
5	1:2.88	+104	+5.2x10^{3}	+5.74x10^{3}
6	1:3.96	+110	+5.2(5)x10^{3}	+5.75x10^{3}

[*] Chemical Shifts from $S_2O_5F_2$ (internal) at 56.4 M c/s.

and 65.0°C./20 m.m. respectively. The F^{19} n.m.r. spectra of these two samples showed very distinctly the three resonance peaks, and the relative intensities of these peaks were fairly close to the ratio 3:2:1 (Table 4). All the other mixtures were distilled under atmospheric pressure and the constant-boiling mixtures so obtained gave spectra in which the relative intensities of the three peaks were generally not very close to the ratio 3:2:1. In some cases, the two As-F peaks overlapped to a small extent presumably because of the presence of traces of unreacted arsenic trifluoride which probably facilitates the slow fluorine-exchange between $AsF_2(SO_3F)$ and $AsF(SO_3F)_2$.

Table 4 gives a list of compositions of the various samples of the constant-boiling mixture, which were deduced for each sample from the corresponding values of relative intensities of the n.m.r. peaks. The composition of each sample was formulated as $AsF_3:xSO_3$ and was found to agree with the empirical formula $AsF_3.1.5SO_3$ to within about 5 per cent. The most striking deviation from $AsF_3.1.5SO_3$, of +11%, occurred with the sample obtained from the 1:3.96 mixture in which sulphur trioxide was in large excess and the distillate was found to consist of more $AsF(SO_3F)_2$ than $AsF_2(SO_3F)$.

Three samples of the constant-boiling mixture (Samples 1, 4 and 6 in Table 4) were analysed chemically for fluorine and sulphur. Of these samples, Sample 1

TABLE 4 SAMPLES OF THE CONSTANT-BOILING MIXTURE OBTAINED FROM DIFFERENT INITIAL MIXTURES AND UNDER DIFFERENT CONDITIONS

Constant Boiling Mixtures		Pressure	Boiling Points °C.	Relative Intensities of n.m.r. Peaks			Composition of Sample		
Sample No.	From Initial AsF_3-SO_3 Mixture			S-F	$-OAsF_2$	OAsFO	Relative Amounts $AsF(SO_3F)_2 = 1$	$AsF_3:xSO_3$	Deviation from $2AsF_3:3SO_3$
1	1:1.01	12 mm	55.5	3.26 ±0.08	1.94 ±0.01	1	0.97 $AsF_2(SO_3F)$ 1 $AsF(SO_3F)_2$ 0.10 $As(SO_3F)_3$	1:1.58	5.3%
2	1:1.52	atm	138.2	3.73 ±0.07	2.85 ±0.03	1	1.40 $AsF_2(SO_3F)$ 1 $AsF(SO_3F)_2$ 0.10 $As(SO_3F)_3$	1:1.48	-1.3%
2a	1:1.5	atm	139 to 139.5	3.35 ±0.09	2.83 ±0.04	1	1.41 $AsF_2(SO_3F)$ 1 $AsF(SO_3F)_2$ 0.01 $As(SO_3F)_3$	1:1.42	-5.3%
3	1:2.01	20 mm	65.0	3.14 ±0.04	1.90 ±0.03	1	0.93 $AsF_2(SO_3F)$ 1 $AsF(SO_3F)_2$ 0.07 $As(SO_3F)_3$	1:1.57	4.7%

TABLE 4 Cont'd. SAMPLES OF THE CONSTANT-BOILING MIXTURE OBTAINED FROM DIFFERENT INITIAL MIXTURES AND UNDER DIFFERENT CONDITIONS

Constant Boiling Mistures		Pressure	Boiling Points °C.	Relative Intensities of n.m.r. Peaks			Composition of Sample		
Sample No.	From Initial AsF_3-SO_3 Mixture			S-F	$-OAsF_2$	OAsFO	Relative Amounts $AsF(SO_3F)_2 = 1$	$AsF_3:xSO_3$	Deviation from $2AsF_3:3SO_3$
4	1:2.46	atm	138.5 to 139	3.74 ±0.10	2.72 ±0.01	1	1.33 $AsF_2(SO_3F)$ 1 $AsF(SO_3F)_2$ 0.13 $As(SO_3F)_3$	1:1.52	1.3%
4a	1:2.5	atm	140	3.82 ±0.08	2.64 ±0.01	1	1.33 $AsF_2SO_3F)$ 1 $AsF(SO_3F)_2$ 0.17 $As(SO_3F)_3$	1:1.54	2.7%
5	1:2.88	atm	138 to 139	3.60 ±0.08	2.38 ±0.03	1	1.18 $AsF_2(SO_3F)$ 1 $AsF(SO_3F)_2$ 0.14 $As(SO_3F)_3$	1:1.54	2.7%
6	1:3.96	atm	137.5 to 138.5	3.40 ±0.04	1.53 ±0.07	1	0.75 $AsF_2(SO_3F)$ 1 $AsF(SO_3F)_2$ 0.40 $As(SO_3F)_3$	1:1.72	11.4%

was obtained from the 1:1.01 mixture distilled under reduced pressure; Sample 4 was obtained from the 1:2.46 mixture fractionally distilled under atmospheric pressure; and Sample 6 was obtained from the 1:3.96 mixture distilled under atmospheric pressure. From the mean values of these analytical results, a composition, $AsF_3:xSO_3$, was calculated for each sample, and was then compared with the composition deduced from n.m.r. results. The results are given below:

SAMPLE	CALCULATED FROM NMR DATA			FOUND BY CHEMICAL ANALYSIS		
	F%	S%	COMPOSITION	F%	S%	COMPOSITION
1	22.06	19.63	$AsF_3.1.58SO_3$	21.58 21.73	19.56 19.58	$AsF_3.1.61SO_3$
4	22.33	19.36	$AsF_3.1.54SO_3$	22.30 22.26	19.28 19.33	$AsF_3.1.54SO_3$
6	21.14	20.48	$AsF_3.1.73SO_3$	20.75 20.49	19.46 19.71	$AsF_3.1.68SO_3$

An attempt was made to split the S-F peak by dissolving a sample of the constant-boiling mixture (Sample 4 in Table 4) in a suitable solvent and then observing the n.m.r. spectrum at low temperature. Liquid sulphur dioxide (m.p. -72.7°C.) was chosen as the solvent and a 25% solution (by volume) was prepared for the experiment. At room temperature, the spectrum showed, besides the two As-F peaks, one peak in the S-F region with a peak width of

5.1 c/s. At -65°C., there was still one peak in the S-F region, but it became as wide as 36 c/s. At temperature lower than -65°C., the signal started to diminish and disappear probably because the solution became highly viscous at such temperatures, and no splitting of the S-F peak was observed.

(ii) Other Evidence

Cryoscopic measurements on dilute solutions of the distillate (Sample 4 in Table 4) in fluorosulphuric acid (14) gave an apparent molecular weight slightly less than half of the value required by the empirical formula $2AsF_3.3SO_3$. (Table 5). Taking into account the non-ideality of the solution, it is reasonable to assume that at infinite dilution the apparent molecular weight would have a value close to 253.6, as required by the composition of Sample 4. The electrical conductance of the solution showed no significant difference from that of pure fluorosulphuric acid, indicating that the supposed compound $2AsF_3.3SO_3$ does not undergo ionization in fluorosulphuric acid. Vapour-density measurements, at 90^oC. and lower, on various samples gave values of molecular weight close to the value 252 (Table 6). At higher temperatures and pressures, the values of apparent molecular weight became much less than 252. The most reasonable interpretation of these results is that the supposed compound $2AsF_3.3SO_3$ actually consists of a constant-boiling mixture of approximately equal amounts of $AsF_2(SO_3F)$ and $AsF(SO_3F)_2$; and the interpretation of the low values of apparent weight obtained from the vapour-density measurements above 90^oC. is probably that at these temperatures there is some dissociation of $AsF_2(SO_3F)$ and $AsF(SO_3F)_2$ in the vapour state into AsF_3 and SO_3.

TABLE 5 CRYOSCOPIC RESULTS IN HSO_3F

WEIGHT OF SAMPLE, g.	WEIGHT OF HSO_3F, g	FREEZING POINT DEPRESSION, C°	APPARENT MOLECULAR WEIGHT
1.8199	165.34	0.150	249
3.3890	166.49	0.305	227
5.1974	167.78	0.475	222
6.8675	168.99	0.637	217
9.5302	170.91	0.885	214

Molecular Weights: $2AsF_3.3SO_3$ = 504

Sample 4, $AsF_3.1.52SO_3$ = 253.6

TABLE 6 VAPOUR-DENSITY MEASUREMENTS

WEIGHT OF SAMPLE, g.	PRESSURE, m.m. Hg	TEMPERATURE °C	APPARENT MOLECULAR WEIGHT
0.210	52.5	83	256
0.205	53.2	86	249
0.270	74.9	90	235
0.270	89.7	94	200
0.354	132.3	106	182

(iii) Attempts to Isolate the Components

Attempts were made to isolate the components of the constant-boiling mixture by distilling arsenic trifluoride-sulphur trioxide mixtures. An AsF_3-SO_3 mixture of mole ratio 1:1.66 was divided into several portions and each portion was distilled at a different pressure. In this mixture, $AsF_2(SO_3F)$ and $AsF(SO_3F)_2$ would be expected to be produced in approximately equal amounts. When the distillation was carried out under atmospheric pressure distillates collected at a number of convenient boiling ranges all showed two As-F peaks in the F^{19} n.m.r. spectrum. The constant-boiling mixture boiled at 138.5°C. When the distillation was carried out under a pressure of 80 m.m. Hg the first milliliter of distillate was collected from room temperature up to a boiling point of 81°C. The n.m.r. spectrum of this distillate at room temperature showed one As-F peak at the position of $-OAsF_2$ groups; but, at -55°C., a small peak appeared in the spectrum at the position of -OAsFO- groups in addition to the $-OAsF_2$ peak. All other fractions of distillate collected at higher temperatures showed two As-F peaks in the spectrum at room temperature. Similar results were obtained when the distillation was carried out under a pressure of 30 m.m. Hg. The constant-boiling mixture boiled at

91°C./80 m.m. and 74°C./30 m.m.

Another AsF_3-SO_3 mixture with a mole ratio of 1:0.715 was fractionally distilled under atmospheric pressure. In this mixture, arsenic trifluoride was present in excess, and the F^{19} n.m.r. spectrum of this liquid consisted of one S-F peak and one intense As-F peak. (Compare with Chapter 111, section (ii).) On distillation of this mixture, the first two fractions of distillate collected from room temperature to 57.8°C. and from 57.8°C. to 58.0°C. showed no S-F signals in the n.m.r. spectrum, but an intense As-F signal. Since pure arsenic trifluoride boils at 58.0°C., this As-F signal is undoubtedly due to unreacted arsenic trifluoride which was present in excess and distilled off first. After this fraction, the temperature rose rapidly from 58.0°C. to 139°C., and only a few drops of distillate were collected within this boiling range. The n.m.r. spectrum still showed an intense As-F signal, but in the S-F region, a very small signal appeared. When the spectrum was observed at -55°C., the As-F signal split off a small peak which was about 175 c/s to high field of the AsF_3 signal and at the position of the $-OAsF_2$ signal. The next two fractions were collected between 139°C. and 139.8°C., and between 139.8°C. and 140°C., and their n.m.r. spectra showed that they consisted of the constant-boiling mixture of $AsF_2(SO_3F)$ and $AsF(SO_3F)_2$.

While the constant-boiling mixture can be obtained by distilling arsenic trifluoride-sulphur trioxide mixtures under reduced pressure, it can be broken up into fractions having different compositions by subjecting the constant-boiling mixture itself to similar treatments. A sample of the constant-boiling mixture was divided into three portions and was distilled under pressures of 100, 20 and 6 m.m. Hg respectively. The results from the n.m.r. spectra of the fractions of distillate are tabulated in Table 7. It appeared from the n.m.r. spectra of distillates obtained at pressures of 100 and 20 m.m. Hg that pure $AsF_2(SO_3F)$ could be obtained if only the first few drops of distillate were examined. In an attempt to achieve this, a distillation was carried out under a pressure of 62 m.m. Hg. The n.m.r. spectrum at room temperature of the first drops of liquid showed one peak in the S-F region and one peak in the As-F region, at the position of $-OAsF_2$ groups; however, at -55°C., a small peak appeared in the As-F region in addition to the $-OAsF_2$ peak. This small peak did not appear at the position of -OAsFO- groups, but at the position of unreacted arsenic trifluoride. Thus this procedure not only failed to achieve the isolation of one of the components, but it also brought about some decomposition of the components into the reactants.

A fractional distillation of the AsF_3-SO_3 mixture of mole ratio 1:2.46 was also carried out. In this mixture, sulphur trioxide was present in excess and unreacted

TABLE 7 RE-DISTILLATION OF THE CONSTANT-BOILING MIXTURE

PRESSURE FOR DISTILLATION	BOILING POINTS	F^{19} N. M. R. SPECTRA			COMPOSITION (RELATIVE AMOUNTS) $AsF(SO_3F)_2 = 1$
		TEMPERATURE	SIGNAL	RELATIVE INTENSITIES	
Before Distillation		Room Temp.	S-F	3.65 ± 0.15	1.29 $AsF_2(SO_3F)$
			$-OAsF_2$	2.58 ± 0.05	1 $AsF(SO_3F)_2$
			-OAsFO-	1	0.12 $As(SO_3F)_3$
100 mm	Room Temp. to 93.5	Room Temp.	S-F	0.729 ± 0.005	
			As-F	1	4.38 $AsF_2(SO_3F)$
		-55°C	S-F	6.38 ± 0.10	1 $AsF(SO_3F)_2$
			$-OAsF_2$	8.77 ± 0.08	
			-OAsFO-	1	
	93.5 to 95	Room Temp.	S-F	2.92 ± 0.07	0.73 $AsF_2(SO_3F)$
			$-OAsF_2$	1.46 ± 0.01	1 $AsF(SO_3F)_2$
			-OAsFO-	1	0.06 $As(SO_3F)_3$
	95	Room Temp.	S-F	2.78 ± 0.04	0.50 $AsF_2(SO_3F)$
			$-OAsF_2$	1.27 ± 0.03	1 $AsF(SO_3F)_2$
			-OAsFO-	1	0.05 $As(SO_3F)_3$

TABLE 7 Cont'd. RE-DISTILLATION OF THE CONSTANT-BOILING MIXTURE

PRESSURE FOR DISTILLATION	BOILING POINTS	F^{19} N. M. R. SPECTRA			
		TEMPERATURE	SIGNAL	RELATIVE INTENSITIES	COMPOSITION (RELATIVE AMOUNTS) $AsF(SO_3F)_2 = 1$
20 mm	Room Temp. to 61	Room Temp.	S-F	0.631 ± 0.008	
			As-F	1	8.33 $AsF_2(SO_3F)$
		-55°C.	S-F	10.5 ± 0.8	1 $AsF(SO_3F)_2$
			$-OAsF_2$	16.7 ± 0.5	
			-OAsFO-	1	
	61 to 65	Room Temp.	S-F	2.78 ± 0.07	0.53 $AsF_2(SO_3F)$
			$-OAsF_2$	1.04 ± 0.04	1 $AsF(SO_3F)_2$
			-OAsFO-	1	0.08 $As(SO_3F)_3$
	65	Room Temp.	S-F	2.78 ± 0.12	0.36 $AsF_2(SO_3F)$
			$-OAsF_2$	0.72 ± 0.01	1 $AsF(SO_3F)_2$
				1	0.02 $As(SO_3F)_3$

TABLE 7 Cont'd. RE-DISTILLATION OF THE CONSTANT-BOILING MIXTURE

PRESSURE FOR DISTILLATION	BOILING POINTS	F^{19} N.M.R. SPECTRA			
		TEMPERATURE	SIGNAL	RELATIVE INTENSITIES	COMPOSITION (RELATIVE AMOUNTS) $AsF(SO_3F)_2 = 1$
6 mm	Room Temp. to 52	Room Temp.	S-F	4.19 ± 0.17	1.83 $AsF_2(SO_3F)$
			$-OAsF_2$	3.66 ± 0.15	1 $AsF(SO_3F)_2$
			-OAsFO-	1	0.12 $As(SO_3F)_3$
	52 to 54	Room Temp.	S-F	2.80 ± 0.04	0.5 $AsF_2(SO_3F)$
			$-OAsF_2$	0.99 ± 0.04	1 $AsF(SO_3F)_2$
			-OAsFO-	1	0.1 $As(SO_3F)_3$

sulphur trioxide composed the first fraction of distillate which boiled at 44.5°C. and gave no signal in the F^{19} n.m.r. spectrum. The fractions collected below the boiling point 123°C. gave similar spectra. There were no signals in the As-F region; but in the S-F region, the signals consisted of four peaks which could be identified as polysulphuryl fluorides:

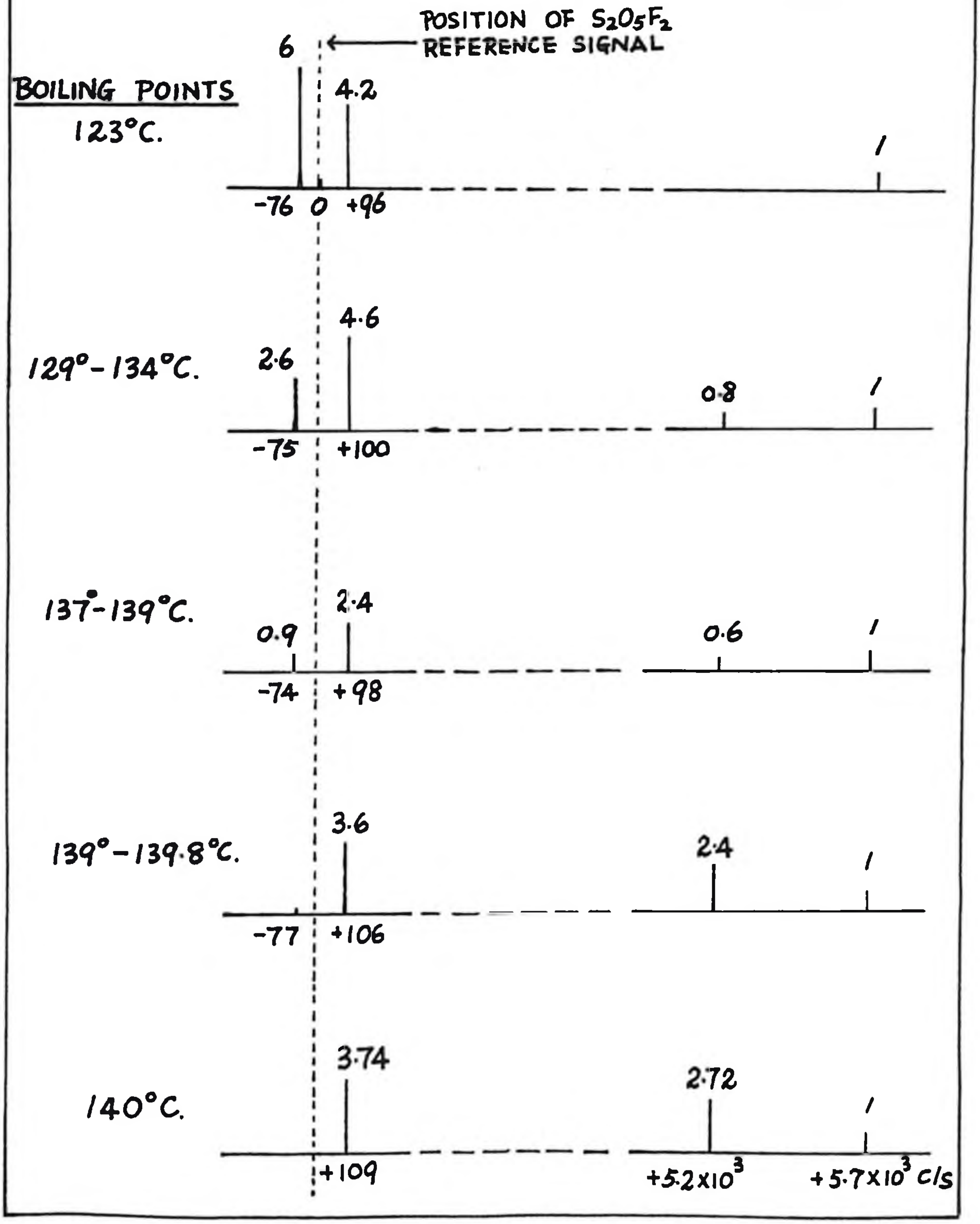
CHEMICAL SHIFTS*	-118	-109	-80	0
POLYSULPHURYL FLUORIDES	$S_5O_{14}F_2$	$S_4O_{11}F_2$	$S_3O_8F_2$	$S_2O_5F_2$

*Chemical Shifts from $S_2O_5F_2$ (internal) in c/s at 56.4 M c/s.

and one peak at +44 c/s which was assigned to $-SO_3F$ groups in $As(SO_3F)_3$. At a boiling point of 123°C. and above, As-F peaks started to appear. For the fraction which boiled at 123°C., the spectrum showed one peak in the As-F region at the position of -OAsFO- groups, and in the S-F region two large and one small peaks. (Spectra are represented in Figure 10, each peak by one vertical line, and its relative intensity by the number immediately above the line.) The small peak appeared at 0 c/s and was due to disulphuryl fluoride. Of the two large peaks, the one at lower field was considered to be due to trisulphuryl fluoride and the one at higher field to $-SO_3F$ groups in $AsF(SO_3F)_2$. A second As-F peak appeared in the spectrum of the fraction which boiled between 129° and 134°C. This peak appeared at lower field by about 540 c/s and was at the position of $-OAsF_2$ groups; its intensity was rather low, but increased in the higher-boiling fractions. There were still two main S-F peaks of which the one at lower field gradually decreased in intensity as the boiling point of the fractions increased; until at a boiling point of 139.8°C., the spectrum of this fraction showed in the S-F region only one main peak at +106 c/s and one small peak at -77 c/s. The position of this small peak agreed with the chemical shift for trisulphuryl fluoride, and the main peak eventually became the S-F peak in the spectrum of the constant-boiling mixture which boiled at 140°C. This sample of the constant-boiling mixture had a composition of 1.33 $AsF_2(SO_3F)$, 1 $AsF(SO_3F)_2$ and 0.13 $As(SO_3F)_3$, (Table 4).

The spectrum was also studied at -27°C. for the fraction which boiled between 137° and 139°C. At room temperature, the spectrum showed two S-F signals. At -27°C., it showed three S-F signals at approximately -79, -39 and +105 c/s. The peak at -79 c/s agreed with the chemical shift for trisulphuryl fluoride; the peak at +105 c/s agreed with that for $-SO_3F$ groups; but the interpretation of the peak at -39 c/s is uncertain, one possibility being that it could be due to the formation

FIGURE 11 DIAGRAMMATIC REPRESENTATION OF N.M.R. SPECTRA OF FRACTIONS OF DISTILLATE AT 123°C. AND ABOVE FROM 1:2·46 MIXTURE. CHEMICAL SHIFTS IN C/S FROM $S_2O_5F_2$ (INTERNAL) AT 56·4 Mc/s



of $-S_2O_6F$ groups. However, these two peaks at lower field seemed to merge into one at room temperature, and trisulphuryl fluoride has not been previously found to undergo fluorine-exchange with any other compound.

Neither of the main components of the constant-boiling mixture was isolated in a pure state in any of these experiments.

CHAPTER V SUMMARY

Evidence has been obtained that the supposed compound $2AsF_3$-$3SO_3$ is in fact a constant-boiling mixture containing mainly $AsF_2(SO_3F)$ and $AsF(SO_3F)_2$, even though it did not prove possible to isolate either of the components in a pure state. The strongest evidence was obtained from the relative intensities of the signals in F^{19} n.m.r. spectra ______ the relative intensities of the three peaks were not found to be in very good agreement with the ratio 3:2:1 as claimed by Muetterties and Coffman. These relative intensities varied from sample to sample, and so did the corresponding composition for each sample, showing a marked dependence on the pressure under which the liquid was obtained by distillation. Finally, the distillate obtained at atmospheric pressure was partially separated by re-distillation under reduced pressures into fractions which contained varying amounts of $AsF_2(SO_3F)$ and $AsF(SO_3F)_2$. This can only be explained if the liquid is assumed to be a constant-boiling mixture, the main components of which are $AsF_2(SO_3F)$ and $AsF(SO_3F)_2$. The apparent molecular weight of this material in fluorosulphuric acid and in the vapour state is also in agreement with the conclusion that it is a mixture of $AsF_2(SO_3F)$ and $AsF(SO_3F)_2$.

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