I. DISTRIBUTION OF ANTIMONY (III) BETWEEN HYDROCHLORIC ACID AND ISOPROPYL ETHER

II. THE INFRARED SPECTRA AND PROBABLE STRUCTURES OF SOME NITROGEN-SULFUR COMPOUNDS

Thesis by

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Abstract

Antimony (III) was extracted by isopropyl ether from solutions of HCl, HCl-$HClO_4$, and HCl-NaCl. The ether and acid layers were analyzed for antimony (III) and chloride. On the basis of the variation of the distribution ratios with the aqueous HCl concentrations a model of the species of antimony (III) present in the HCl solution was constructed. The following constants relating the species to one another were calculated.

$$K_{2-3} = \left[SbCl_3\right] a_{H_2O} / \left[SbCl_2OH\right] a^2_{HCl} = 0.145$$
$$K_{3-4} = \left[SbCl_4^-\right] / \left[SbCl_3\right] a_{HCl} = 0.34$$
$$D_2 = \left[SbCl_2OH\right]_e / \left[SbCl_2OH\right]_a = 0.0080$$
$$D_3 = \left[SbCl_3\right]_e / \left[SbCl_3\right]_a = 0.062$$

Spectrophotometric measurements on antimony (III) in acid and ether solutions indicated the presence of a hydrate of $SbCl_3$ in the acid. Reasonable agreement was found between the results predicted by the model and the experimental values of the solubility of $Sb_4O_5Cl_2$ in HCl, the potential of the antimony (III) - antimony (V) half cell in HCl, and the catalytic effect of antimony (III) on the hydrolysis of $SbCl_6^-$.

The infrared spectra of the products of fluorinations of N_4S_4 were taken. CCl_4, $CFCl_3$, SO_2, SOF_2, SF_4, SF_6 and SiF_4 were identified as components of the mixture. Bands of four unknown compounds were found. Compound A with bands at 1375 and 644 cm^{-1} was identified as SNF on the basis of its instability and infrared spectrum. Compound B was identified as NSF_3 since it was not decomposed by heating nor was capable of being further fluorinated. The envelopes of the 1520, 819, and 774 cm^{-1} bands indicate that it is a symmetric rotor. Compound C with bands at 1340 and 1160 cm^{-1} was unidentified. Compound D with bands at 1340 and 1160 cm^{-1} was at first thought to be NSF but a force constant calculation led to an

unreasonable structure. It is still unidentified.

An approximate normal coordinate treatment of SNF led to $k_{NS}=10.4$ millidynes/A and $k_{NF}=2.3$ millidynes/A. These values indicate that the N-F bonding has considerable ionic character. Approximate force constants for NSF_3 were calculated and were found to correspond to the NSF_3 structure with normal single and triple bonds.

No evidence was found for the existence of Glemser's SN_2F_2. His erroneous results could be explained by the presence of SO_2, SOF_2, and SF_4 as impurities in his product of the N_4S_4 fluorination.

PART I

DISTRIBUTION OF ANTIMONY (III) BETWEEN HYDROCHLORIC ACID AND ISOPROPYL ETHER

DISTRIBUTION OF ANTIMONY (III) BETWEEN HYDROCHLORIC ACID AND ISOPROPYL ETHER

I. Introduction

The extraction of antimony (III) and (V) from hydrochloric acid solutions by isopropyl ether has been investigated by Edwards and Voigt (1); they found that antimony (III) was extracted by isopropyl ether and their results indicated that the species of antimony (III) in such solutions might be determined by a study of the distribution measurements.

Neumann has made a determination of the antimony (V) species in HCl solutions by spectrophotometric methods (2). Unfortunately that method is not applicable to the investigation of the antimony (III) species as their absorption peaks in general lie in the vacuum ultraviolet region.

Previous indications as to the antimony (III) species present in 2VF (volume formal, formula weights per liter of solution) to 6VF hydrochloric acid have been found by potentiometric and polarographic methods. Swift and Brown investigated the potential of the antimony (III)-antimony (V) half cell in 2VF to 6VF HCl and suggested that the oxidizable species was $SbCl_4^-$ (3). Haight made a polarographic study of the effect of Cl^- on the half-wave potential of antimony (III) and concluded that $SbCl_4^-$ was the reducible species present in 4F HCl (4). These conclusions have the limitation that they only detect the presence of one chemically active species and give no information on the nature of the other species.

Neumann (5) measured the hydrolysis kinetics of antimony (V) species and found that antimony (III) catalyzed the reaction

$$SbCl_6^- + H_2O = SbCl_5(OH)^- + H^+Cl^-$$

The catalysis was more effective at lower HCl concentrations and from this behavior he suggested that $SbCl_3$ was the active catalytic species. From his data it is possible to calculate the per cent of the antimony (III) present as this active species.

Whitney and Davidson (6) found that they could explain the interaction absorption of antimony (III) and antimony (V) in strong HCl (10VF) by the presence of a "collision complex" but they observed no such a complex in 3.5VF HCl. In this connection Edwards and Voigt (1) found that antimony (V) was 98-100% extracted from solutions 3-6F in HCl (ether to acid volume ratio was 2.5) when antimony (III) was absent but was only 20-70% extracted when antimony (III) was present. Neumann (2) has shown that a hexachloro antimony (V) species is extracted because the absorption spectrum of the ether extracts of 3VF and 11.45VF HCl solutions of antimony (V) was the same as the spectrum of the 11.45VF HCl solution. He concluded that the lesser chlorinated species were not extracted. One can conclude that the lesser extraction of antimony (V) when antimony (III) is present is a consequence of the antimony (III) catalyzed hydrolysis of the extractable to a non-extractable species.

The experimental work performed in this investigation was simple. Antimony (III) at various concentrations in different solutions was distributed between isopropyl ether and these solutions. The antimony (III) and chloride concentrations were measured in both phases. A few experiments were carried out to test the distribution of antimony (III) between HCl solutions and miscellaneous solvents. Some spectrophtometric studies were done on antimony (III) solutions in HCl and in solutions of H_2SO_4 and KBr.

II. Preparation of reagents

An antimony (III) stock solution, 0.85VF in $SbCl_3$ was prepared by dissolving reagent grade $SbCl_3$ in 5.8VF HCl. The solution was tested for antimony (V) by adding KI to equal amounts of stock solution and 5.8VF HCl. Known iodine solution was added to the HCl solution until its CCl_4 extract matched that of the stock solution. Antimony (V) was found to less than 0.02%.

Pure grade isopropyl ether was distilled with hydroquinone present to prevent formation of peroxides. The fraction boiling at 67.2° to 68.2°C (uncorrected) was taken and stored over sodium metal.

Standard KI_3, $AgNO_3$, KSCN, and NaOH were prepared by conventional analytical methods.

Mercuric thiocyanate was made from reagent grade $Hg(NO_3)_2$ and KSCN and purified by recrystallization from water. A solution for the colorimetric determination of chloride was prepared by dissolving 0.3g of $Hg(SCN)_2$ in 100ml of ethanol.

A 0.04VF solution of potassium tartrate was made from the reagent grade hemihydrate.

III. Distribution measurements

The antimony stock solution was diluted with water and HCl to give the antimony (III) and HCl solutions of the desired concentrations. The stock solution was diluted with an HCl-NaCl solution or an $HClO_4$-HCl solution to make solutions with total Cl^- of 5VF or total H^+ of 5VF. Fifty milliliters of the resultant solution and fifty milliliters of isopropyl ether were placed in a 100ml graduated cylinder and rocked back and forth 100 times. All experiments were carried out in duplicate. The cylinder was then placed in a 30°C bath or allowed to stand at room temperature for several hours. At the end of this time two 10ml samples of the ether were withdrawn with a calibrated pipet and each was extracted twice in a separatory funnel with 10ml portions of tartrate solution; these two tartrate extracts from each sample were combined. Phenolphthalein was added to the solutions from each sample and they were titrated with standard NaOH. One of the neutralized solutions was titrated with standard $AgNO_3$ to determine chloride by the method described by Swift, Arcand, Lutwack, and Meier (7). This method was modified by the use of a large excess of perchloric acid instead of nitric acid to minimize the yellow color of the ferric tartrate complexes which otherwise would obscure the end point. The concentration of nitric acid required to do this was sufficient to oxidize the thiocyanate. In some experiments a colorimetric method for chloride suggested by Ozawa et al., (8) was used. A Klett-Summerson colorimeter was used to determine the absorption of ferric thiocyanate formed when Cl^- liberated SCN^- from $Hg(SCN)_2$ in a ferric nitrate solution. For this method a calibration was made and it was redetermined every time the potassium tartrate, ferric nitrate, or nitric acid solutions were changed.

The other solution from the base titration was acidified with a drop of 6VF HNO_3 with buffered bicarbonate and titrated with standard triiodide solution to a starch end point to determine the antimony (III).

Two 1.00ml samples of the acid layer from each cylinder were taken with a calibrated pipet and added to concentrated tartrate solutions. Each of these was titrated with NaOH and subsequently with KI_3.

IV. Calculation of Distribution Ratios.

Hereafter a symbol enclosed by parentheses indicates a volume formal concentration; a symbol in brackets indicates a volume molal concentration. The symbol C indicates the total concentration of an element in moles per liter, as determined by analysis. The subscript e or a indicates an ether or aqueous phase respectively. D is the distribution ratio, C_{Sb_e}/C_{Sb_a}, and n is the average number of chlorides attached to an antimony. γ is the symbol for an activity coefficient.

The determination by distribution measurements of the species in which an element is present in aqueous solutions is difficult because of the necessity of finding conditions where only one particular species is present in significant concentrations in both phases. In this study unfortunately no such conditions were found. Therefore recourse was made to the treatment of Rossotti, Irving, and Williams (9), bearing in mind the limitation that it is applicable only to ideal systems.

The distribution ratios C_{Sb_e}/C_{Sb_a}, were calculated from the analytically measured concentrations of antimony (III) in the ether and aqueous phases. The results are recorded in Tables Ia, Ib, and Ic and are plotted in Figure I-1. Figure I-2 shows the plots of log D vs. log a_{HCl}. The activities of pure HCl are the values of Randall and Young (10); the activities of HCl in solutions of HCl and NaCl are those of Hawkins (11). Activity coefficients of HCl in the solutions of HCl and $HClO_4$ were calculated from Harned's rule, (12)

$$\log \gamma_{HCl} = \log \gamma_{HCl(0)} + \alpha_C m_C \qquad (1)$$

where m_C is the concentration of $HClO_4$, α_C is a parameter characteristic of the pair of solutes and of the total volume molality, m, and $\gamma_{HCl(0)}$ is the activity coefficient of HCl of volume molality, m, with no added $HClO_4$. α_C was calculated from Murdock and Barton's data on solutions of HCl and $HClO_4$ (13) assuming that α_C is the same for all total molalities when the $HClO_4$ concentration was less than half of the total molality since this was the case in their investigations. The assumption may not be very rigorous but it is necessary as there are no data on solutions of 5M total molality. The values obtained may not be very accurate but are definitely closer to the actual values of a_{HCl} than assuming that γ_{HCl} is constant.

Table Ia

Distribution of Antimony (III) between Isopropyl Ether and HCl Solutions

$[HCl]_a$	C_{Sb_a}	Number of determinations	Distribution ratio C_{Sb_e}/C_{Sb_a}
4.8	0.42	4	0.0095±.0015
4.96	0.091	3	0.0073±.0002
3.91	0.109	4	0.0112±.0002
3.05	0.115	2	0.0163±.0005
2.18	0.041	4	0.0206±.0005

Table Ib

Distribution of Antimony (III) between Isopropyl Ether and HCl-NaCl Solutions

$[HCl]_a$	$(Cl)^-$	C_{Sb_a}	Number of determinations	Distribution ratio
4.15	4.95	0.102	4	0.0072±.0001
3.35	5.15	0.116	4	0.0075±.0001
3.1	4.8	0.105	3	0.0076±.0001
2.3	4.85	0.085	3	0.0089±.0001

Table Ic

Distribution of Antimony (III) between Isopropyl Ether and HCl-HClO$_4$ Solutions

$[HCl]_a$	(H^+)	C_{Sb_a}	Number of determinations	Distribution ratio
3.9	5.0	0.085	4	0.0150±.0006
2.85	4.85	0.10	4	0.033±.004
2.45	5.05	0.083	2	0.053±.001

Figure I-1. Distribution of Antimony (III) between isopropyl ether and HCl, as a function of the aqueous HCl concentration.

Curve 1. HCl-$HClO_4$ solutions $H^+ = 5F$

Curve 2. HCl

Curve 3. HCl-NaCl solutions $Cl^- = 5F$

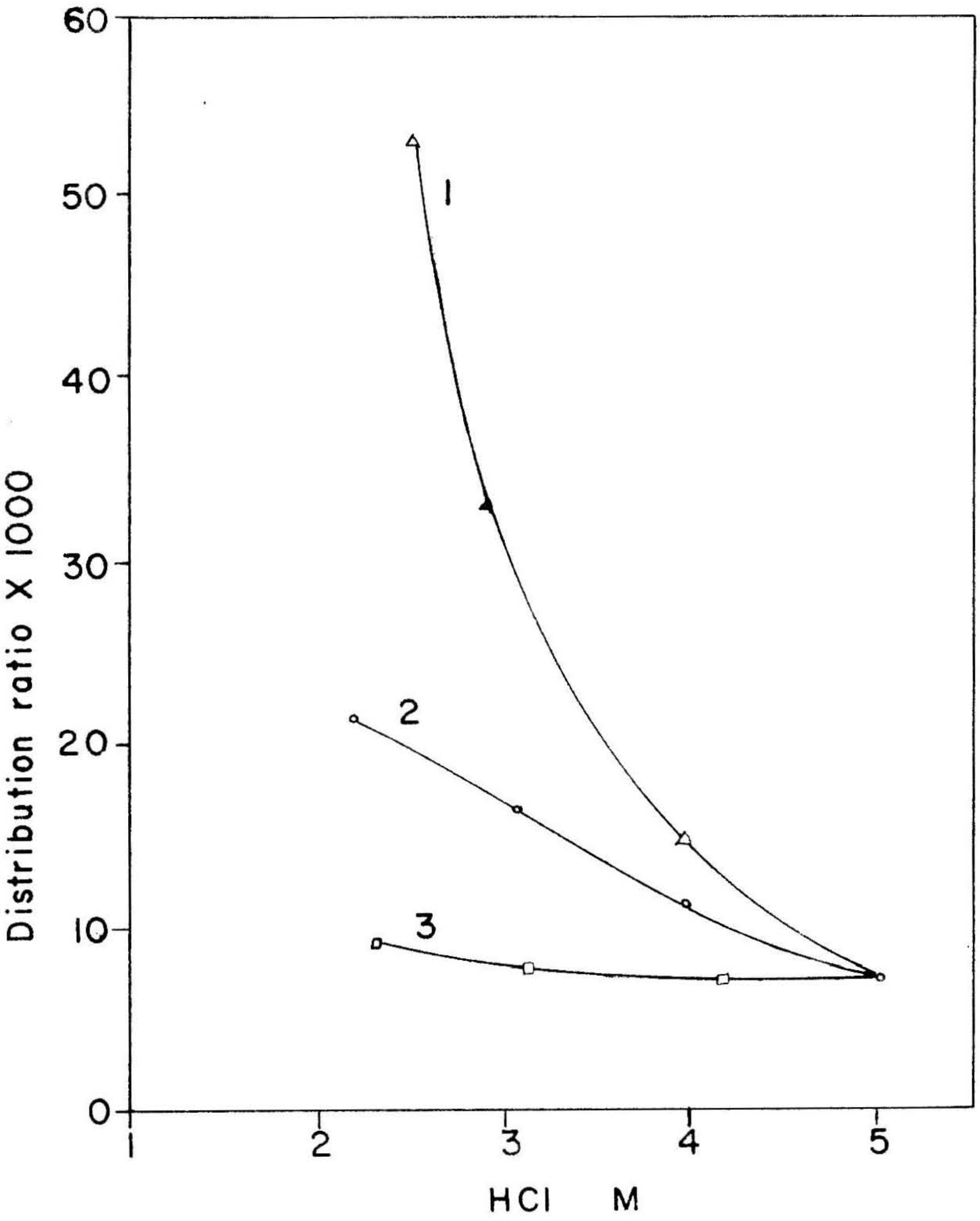


Figure I-1

Figure I-2. Logarithm of the distribution ratio as a function of aqueous HCl activity

Curve 1. HCl-$HClO_4$ solutions H^+ = 5F

Curve 2. HCl

Curve 3. HCl-NaCl solutions Cl^- = 5F

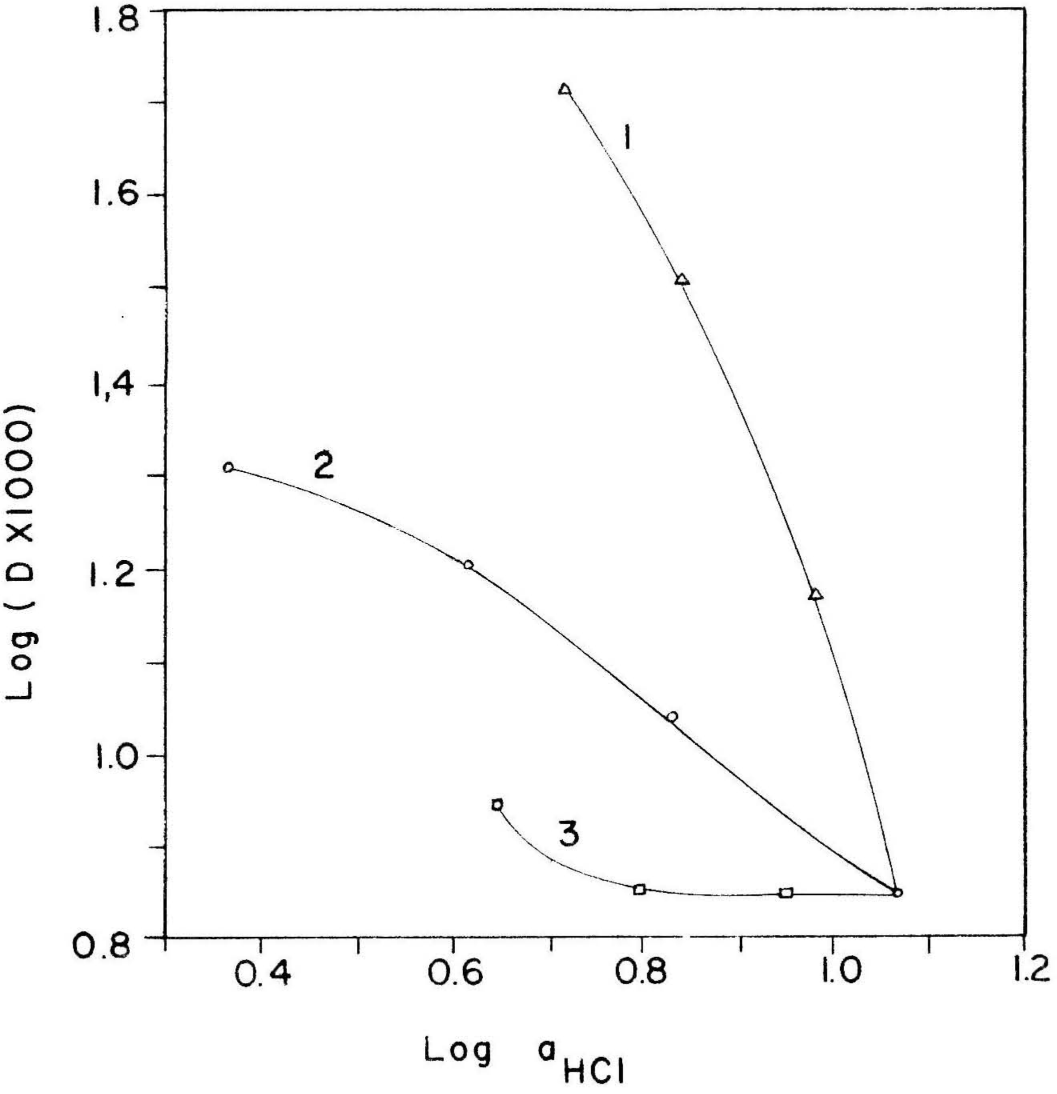


Figure I-2

From Murdock and Barton's data for 1M HCl-$HClO_4$ solutions α_C was calculated to be 0.0071. The values of $\log \gamma_{HCl}$ in Table II were obtained by using this value of α_C in equation 1.

Table II

Calculated Activities of HCl in HCl-$HClO_4$ Solutions

HCl (VF)	$HClO_4$ (VF)	$\log \gamma_{HCl(0)}$	$\log \gamma_{HCl}$	a_{HCl}
4.03	1.02	0.380	0.387	9.8
2.95	1.98	0.365	0.379	7.05
1.96	2.80	0.345	0.365	4.5

According to Rossotti the slope $\dfrac{\partial \log D}{\partial \log a_{HCl}}_{(Cl^-) = \text{constant}}$ is equal to $h_e - h_a$ where h_e is the average number of hydrogens per metal in the ether phase and h_a is the average number of hydrogens attached to each metal atom in the aqueous phase. From Figure I-2 it may be seen that $h_e - h_a$ is essentially zero which means that the same species exist in both phases or that there are more chlorides per antimony in the aqueous phase. For example if $HSbCl_4$ is the predominant species in the ether phase then $HSbCl_4$ or $HSbCl_5^-$ or even $HSbCl_6^=$ may be the main species in the aqueous phase.

Rossotti also derived that $\dfrac{\partial \log D}{\partial \log a_{HCl}}_{(H^+) = \text{constant}} = n_e - n_a$ where the n's are the average number of chlorides per metal atom in the two phases. The value of this slope is calculated from Figure I-2 to be -3. This means that if $HSbCl_4$ is the main species in the ether then $H_xSbCl_7^{x-4}$ predominates in the aqueous phase. This is quite unreasonable, requiring antimony (III) to have a coordination number of seven. That perchloric acid solutions deviate from ideal behavior is shown by the measurements of the distribution of HCl between the ether and the solutions containing

$HClO_4$. If the solutions were ideal the solubility of HCl should depend only on the activity of the HCl. In Table III the observed concentrations of HCl in the ether phase are compared with the concentrations to be expected if the HCl-$HClO_4$ solutions were ideal.

Table III

Comparison of Measured and Calculated Solubilities of HCl in Isopropyl Ether

HCl (VF)	$HClO_4$ (VF)	a_{HCl}	$[HCl]_e$	$[HCl]_e$ ideal
4.03	1.02	9.8	0.00261	0.0016
2.95	1.98	7.05	0.00262	0.00073
1.96	2.80	4.5	0.00244	0.00035

As a check on the values of n_e-n_a and h_e-h_a the slope of log D vs. log a_{HCl} in pure HCl should be the sum of the other two slopes. In 5VF HCl this slope is -0.52 and the sum of the other two slopes is -3. Thus it seems reasonable to exclude the data from the HCl-$HClO_4$ solutions. Since $\frac{\partial \log D}{\partial \log a_{HCl}}{}_{(Cl^-) = \text{constant}}$ is zero then the slope of log D vs. log a_{HCl} in HCl should equal the quantity n_e-n_a. Table IV shows the values of this quantity at various aqueous HCl concentrations.

Table IV

Slope of log D versus log a_{HCl}

$[HCl]_a$	a_{HCl}	n_e-n_a
2.18	2.32	-0.17
3.05	4.15	-0.63
3.91	6.81	-0.88
5.0	11.8	-0.52

With this information it is now possible to calculate n_e. For

$$C_{Cl_e} = [HCl]_e + n_e \, C_{Sb_e} \qquad (2)$$

but $[\mathrm{HCl}]_e$ is a function of $[\mathrm{HCl}]_a$ which in turn is a function of n_a.

$$[\mathrm{HCl}]_a = C_{\mathrm{Cl}_a} - n_a C_{\mathrm{Sb}_a} \tag{3}$$

The C_{Cl_e} and C_{Cl_a} are the concentrations of chloride titrated in samples of the respective phases.

$$C_{\mathrm{Sb}_e} = D C_{\mathrm{Sb}_a} \tag{4}$$

so

$$C_{\mathrm{Cl}_e}/D = [\mathrm{HCl}]_e/D + n_e C_{\mathrm{Sb}_a} \tag{5}$$

Subtracting 5 from 3 gives

$$[\mathrm{HCl}]_a - [\mathrm{HCl}]_e/D = (n_e - n_a)C_{\mathrm{Sb}_a} + C_{\mathrm{Cl}_a} - C_{\mathrm{Cl}_e}/D \tag{6}$$

The amount of chloride attached to the antimony in the ether phase is C_{Cl_e} less $[\mathrm{HCl}]_e$.

Two trial values for $[\mathrm{HCl}]_a$ are taken and the points calculated for $[\mathrm{HCl}]_e$ from equation 6 are plotted on the $[\mathrm{HCl}]_e$ versus $[\mathrm{HCl}]_a$ graph and the line determined by these points is drawn. The intersection of this line and the solubility curve gives the values of $[\mathrm{HCl}]_a$ and $[\mathrm{HCl}]_e$ to be used to obtain the amount of chloride attached to the antimony in the ether phase.

Table V gives the data and calculated values of the various concentrations.

Table V

Distribution Ratios and Chloride to Antimony Ratios as Functions of Aqueous HCl Concentrations

$[\mathrm{HCl}]_a$	C_{Sb_a}	Number of determinations	Distribution ratios (D)	n_a	n_e
2.18	0.041	4	0.0206±.0005	3.04	2.87±.05
3.05	0.115	2	0.0163±.0005	3.61	2.98±.01
3.92	0.109	4	0.0112±.0003	4.02	3.14±.02
5.0	0.094	4	0.0072±.0003	5.2	4.7

The values of n_e indicate that there must be at least three species present in the ether phase when the range of aqueous HCl concentrations is 2-4M. They must have chloride to antimony ratios of two, three, and four. It is reasonable to take them as $SbCl_2OH$, $SbCl_3$, and $HSbCl_4$. The $SbCl_2OH$ is taken in analogy with the species found in the study of arsenic (III) in HCl solutions by Arcand. (14).

An assumption is made at this point; namely that $HSbCl_4$ is completely ionized in the aqueous phase. This requires that the protonated species in the aqueous phase have more chlorides than $SbCl_4^-$ and the next step in the progressively more complexed antimony species therefore would be $HSbCl_5^-$.

The fractions of the total antimony (III) present as the different species in the aqueous and ether phases can be calculated with one further assumption, i.e., that there is no $HSbCl_4$ in the ether extract from the 2.18 M HCl.

In the ether phase over the 2.18 M HCl $C_{Sb_e} = 0.0206\ C_{Sb_a}$ and n_e is 2.87. The antimony (III) in the ether exists only as $SbCl_2OH$ and $SbCl_3$; therefore it is obvious that $\left[SbCl_3\right]_e = 0.87\ C_{Sb_e}$ and that $\left[SbCl_2OH\right]_e =$ $0.13\ C_{Sb_e}$. In the aqueous phase $\left[SbCl_3\right]_a = \left[SbCl_3\right]_e/D_3$ and $\left[SbCl_2OH\right]_a =$ $\left[SbCl_2OH\right]_e/D_2$ where the D's are the respective distribution ratios for the two species.

Now by material balance

$$\left[SbCl_4^-\right]_a = C_{Sb_a} - \left[SbCl_2OH\right]_a - \left[SbCl_3\right]_a \tag{7}$$

Substituting in the values for the last two quantities in equation 7 gives

$$\left[SbCl_4^-\right]_a = C_{Sb_a} - 0.87\ C_{Sb_e}/D_3 - 0.13\ C_{Sb_e}/D_2 \tag{8}$$

In 3.05M HCl

$$\left[HSbCl_5^-\right]_a/C_{Sb_a} = \left[HSbCl_4\right]_e/C_{Sbe} \tag{9}$$

by the requirement that $h_e - h_a = 0$. Let $[HSbCl_4]_e/C_{Sb_e} = x$. In order to have $n_e = 2.98$, $[SbCl_2OH]_e/C_{Sb_e}$ must be $x + 0.02$ and $[SbCl_3]_e/C_{Sb_e}$ must be $0.98-2x$.

In the aqueous phase

$$\frac{[SbCl_2OH]_a}{C_{Sb_a}} = \frac{(x+0.02)\ C_{Sb_e}}{C_{Sb_a}\ D_2} = \frac{(x+0.02)\ D}{D_2} \qquad (10)$$

$$\frac{[SbCl_3]_a}{C_{Sb_a}} = \frac{(0.98-2x)\ D}{D_3} \qquad (11)$$

$$\frac{[SbCl_4^-]_a}{C_{Sb_a}} = - \frac{[SbCl_2OH]_a - [SbCl_3]_a - [HSbCl_5^-]_a}{C_{Sb_a}} \qquad (12)$$

$$n_a = 1/C_{Sb_a} \left\{ 2[SbCl_2OH]_a + 3[SbCl_3]_a + 4[SbCl_4^-]_a + 5[HSbCl_5^-]_a \right\} \qquad (13)$$

Similar equations are derived for the species in 3.91M HCl.

For the reaction

$$SbCl_2OH + H^+Cl^- = SbCl_3 + H_2O \qquad (14)$$

the equilibrium constant, K_{2-3}, is

$$K_{2-3} = \frac{[SbCl_3]_a\ a_{H_2O}}{[SbCl_2OH]_a\ a^2_{HCl}} \qquad (15)$$

Substituting values of the activity of water (10) and HCl in the 2.18M solution and equations 10 and 11 into equation 15 gives

$$K_{2-3} = \frac{D_2(0.87)\ (0.913)}{D_3(0.13)\ (5.38)} = \frac{D_2}{D_3}\ (1.13) \qquad (16)$$

In 3.05M HCl the value of K_{2-3} is

$$K_{2-3} = \frac{D_2(0.98-2x)(0.861)}{D_3(x+0.02)(17.2)} = \frac{D_2(0.98-2x)}{D_3(x+0.02)} = (0.0500) \qquad (17)$$

Equating 16 and 17 and solving for x produces the value x=0.0215.

The same equality is set up for the expression for K_{2-3} in 3.92M HCl and is solved for the fraction of C_{Sb_e} that is present as $SbCl_2OH$. This fraction is found to be 0.013.

It is now possible to solve for D_2 and D_3 since in 2.18M HCl

$$n_a = 3.04 = \frac{2\left[SbCl_2OH\right]_a}{C_{Sb_a}} + \frac{3\left[SbCl_3\right]_a}{C_{Sb_a}} + 4\left\{\frac{1-\left[SbCl_2OH\right]_a-\left[SbCl_3\right]_a}{C_{Sb_a}}\right\} \qquad (18)$$

Equations 10 and 11 are substituted into equation 18 and it is solved for D_2 and D_3.

$$46.6 = \frac{0.26}{D_2} + \frac{0.87}{D_3} \qquad (19)$$

In 3.05M HCl the analogous equation to 18 is set up and solved for D_2 and D_3.

$$25.5 = \frac{0.083}{D_2} + \frac{0.931}{D_3} \qquad (20)$$

The two simultaneous equations 19 and 20 are solved for the values of D_2 and D_3 which are 0.0080 and 0.0621 respectively.

The equations corresponding to 10, 11, and 12 in the 2.18, 3.05, and 3.92M HCl can be solved for the fraction of each species present in the aqueous phase. The results of these calculations are shown in Table VI. The value of n_a in 5M HCl is quite inaccurate since the $\left[HCl\right]_e$ changes rapidly with $\left[HCl\right]_a$ and the distribution ratio is small. This means that small changes in the distribution ratio will produce large changes in n_a.

The equilibrium constants K_{2-3}, K_{3-4}, and K_{4-5} can be calculated with the results given above. The expression for K_{2-3} is equation 15 and its values in the three concentrations of HCl are 0.145, 0.145, and 0.146 respectively.

$$K_{3-4} = \frac{\left[SbCl_4^-\right]_a}{\left[SbCl_3\right]_a \; a_{HCl}} \qquad (21)$$

Table VI

Percent of Antimony (III) Present as Various

Species in HCl and Isopropyl ether

Column I shows the total aqueous antimony (III) concentration; Column II shows aqueous HCl concentration, Column III shows the aqueous HCl activity; Column IV shows the aqueous water activity; Column V shows the average number of chlorides attached to each antimony in the aqueous phase; Column VI shows the average number of chlorides attached to each antimony in the ether phase; Column VII shows the distribution ratio $D = C_{Sb_e}/C_{Sb_a}$.

Under the columns headed "Aqueous" and "Ether" are recorded the per cent of the total antimony in the given phase present as the species designated below.

Aqueous:	Column 2: $SbCl_2OH$	Ether:	Column 2: $SbCl_2OH$
	Column 3: $SbCl_3$		Column 3: $SbCl_3$
	Column 4: $SbCl_4^-$		Column 4: $HSbCl_4$
	Column 5: $HSbCl_5^-$		

C_{Sb_a} I	$[HCl]_a$ II	a_{HCl} III	a_{H_2O} IV	n_a V	Aqueous				Ether			n_e VI	D VII
					2	3	4	5	2	3	4		
0.041	2.18	2.32	0.908	3.04	33.6	28.8	37.6	0	13.	87	0	2.87	0.0206
0.115	3.05	4.15	0.861	3.61	8.45	24.6	64.8	2.15	4.15	93.7	2.15	2.98	0.0163
0.109	3.91	6.81	0.806	4.02	1.8	15.1	67.8	15.3	1.3	83.6	15.3	3.14	0.0112
0.091	4.96	11.6		5.2								4.66	0.0073

The values for this constant in 2.18, 3.05, and 3.92M HCl are 0.564, 0.634, and 0.659.

$$K_{4-5} = \frac{[HSbCl_5^-]_a}{[SbCl_4^-]_a \, a_{HCl}^2} \qquad (22)$$

The values for this constant in 3.05 and 3.92M HCl are 0.0019 and 0.0048.

K_{2-3} is constant for the 2.18 and 3.05M HCl since that was the assumed condition used in the calculations. K_{3-4} is almost constant despite the fact that no correction has been made for the activity coefficient of $SbCl_4^-$. This will be done below. The value of K_{4-5} is not even reasonably constant but this is not surprising. In 3.05M HCl the concentration of $HSbCl_5^-$ is very sensitive to the value of n_e and the accuracy of this quantity is only good to about 2% which would cause changes on the order of 100% in the concentration of this species.

No correction for the activity coefficient of $SbCl_4^-$ has been made. If the activity coefficient is calculated with the equation 23 (14A),

$$\log \gamma = \frac{-0.509\sqrt{I}}{1+1.3\sqrt{I}} \qquad (23)$$

where I is the ionic strength which for HCl solutions is equal to its concentration the new values of K_{3-4} are 0.314, 0.349, and 0.356. These values are still not exact since one of the ions of $HSbCl_4$ is common to the supporting electrolyte and there is no good theoretical equation for calculating activity coefficients a priori for mixtures of electrolytes with a common ion. Nevertheless it is indicative that the species exist in quantities not much different from those calculated.

The value of 5.2 for n_a in 5M HCl indicated the need for a hexachloro species in addition to the others already found. The value of 4.7 for n_e requires the presence of at least H_2SbCl_5 and perhaps even H_3SbCl_6 in the ether phase. With the introduction of the several new species the original problem of distribution studies arises again; namely, that if there are more than two additional species there is not sufficient information to calculate the distribution ratios and equilibrium constants.

An alternative explanation for the large increase in the value of n_e in going from 4M to 5M HCl is that sufficient HCl has dissolved in the ether to change its characteristics to those of a more polar solvent. Ionic species would then distribute more readily into it than into a less polar solvent. With the change in solvent characteristics the relationships derived earlier on the assumption of ideality of the solutions no longer hold.

V. Spectrophotometric measurements

Since the species of antimony (V) in HCl had been determined by spectrophotometric methods it was thought that these methods might be useful in determining the species of antimony (III) in HCl.

Solutions that were 1.5×10^{-4}F in antimony (III) and 1 to 3VF in HCl and a solution 7.5×10^{-4}F in antimony (III) and 4VF in HCl were examined with a Model DU Beckman spectrometer. No peak in the absorption spectrum was observed in the range 220-300mμ.

Isopropyl ether solutions 7.5×10^{-4}F in antimony (III) were prepared by extracting the antimony (III) from 2 and 5M HCl solutions of the appropriate antimony (III) concentrations. These solutions were examined in the range 230-300mμ.

The spectra of antimony (III) in 5VF H_2SO_4 with varying KBr concentrations were examined in the range 230-300mμ.

The spectra observed are shown in Figures I-3 to I-5.

VI. Tests of other solvents

Since isopropyl ether was a poor extractant for antimony (III) in

Figure I-3. Absorption spectra of antimony (III) in HCl solutions

Sb (III) in 1, 2, and 3VF HCl = 7.5×10^{-5}F

Sb (III) in 4VF HCl = 1.5×10^{-4}F

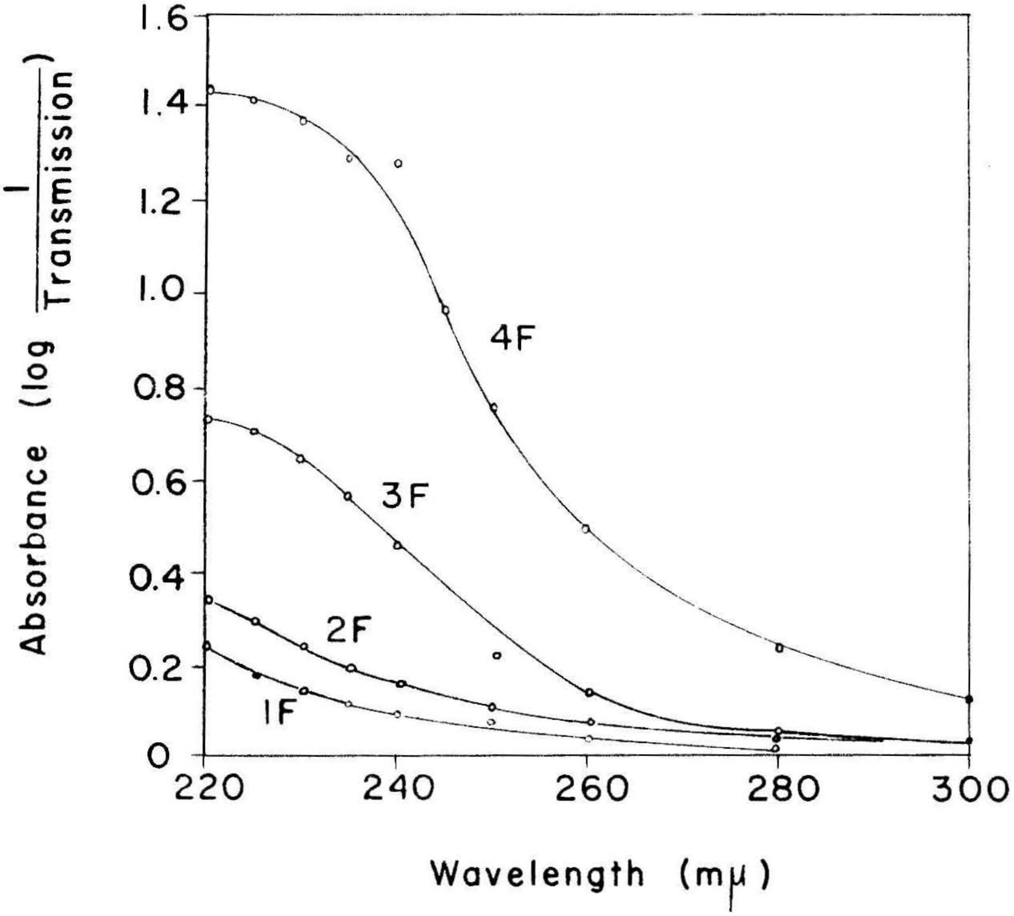

1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
Absorbance (log $\frac{1}{\text{Transmission}}$)
220
240
260
280
300
Wavelength (mμ)
4F
3F
2F
1F

Figure I-3

Figure I-4. Absorption spectra of isopropyl ether solutions of antimony (III) extracted from aqueous HCl. Original aqueous HCl concentration of the solution from which Sb (III) was extracted is noted next to each curve. In the ether Sb (III) = 7.5×10^{-5} F

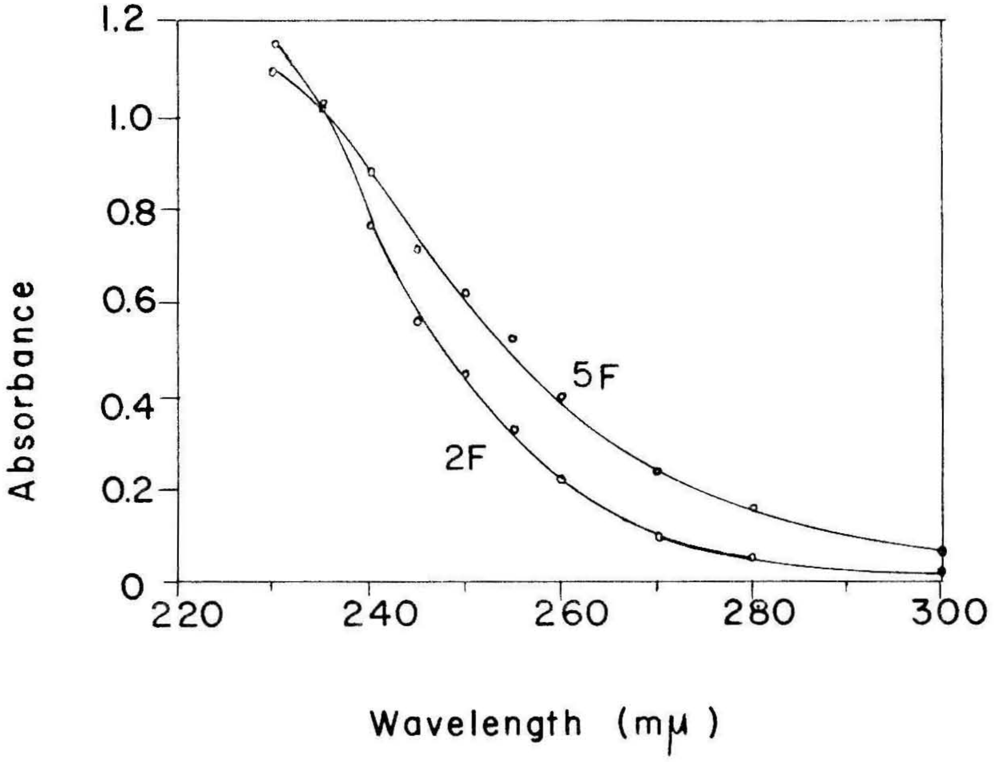

1.2
1.0
0.8
0.6
0.4
0.2
0
Absorbance
220
240
260
280
300
Wavelength (mμ)
5F
2F

Figure I-4

Figure I-5. Absorption spectra of antimony (III)

in H_2SO_4-KBr solutions

H_2SO_4 = 5VF Sb (III) = 1.1×10^{-4}F

KBr concentration

Curve 1. KBr = 2.5×10^{-3}VF

Curve 2. KBr = 1.25×10^{-2}VF

Curve 3. KBr = 2.25×10^{-2}VF

Curve 4. KBr = 3.25×10^{-2}VF

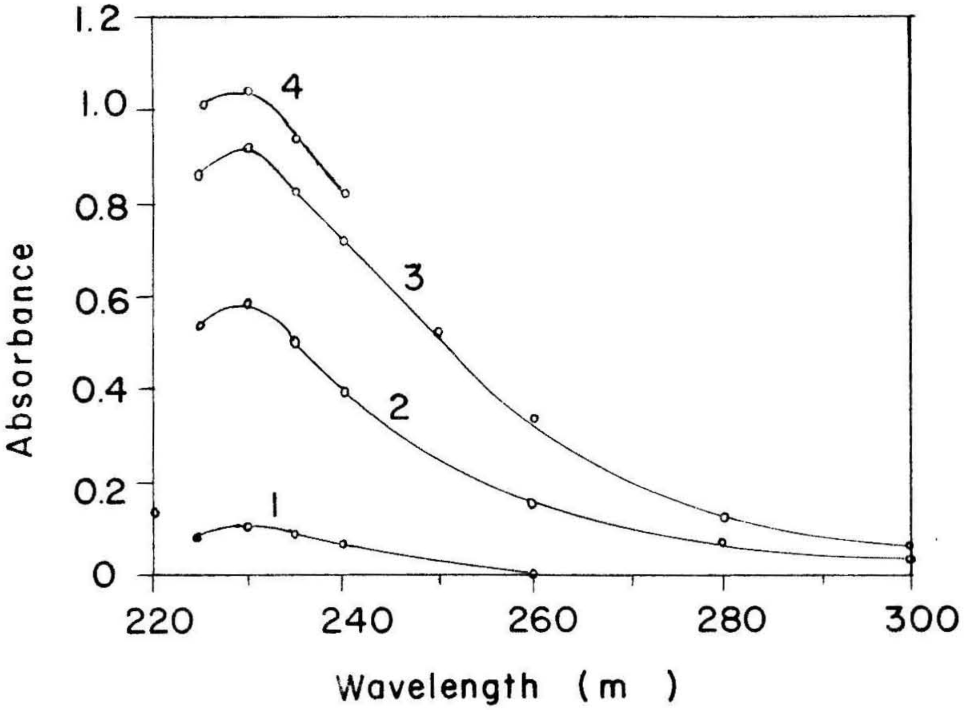

1.2
1.0
0.8
0.6
0.4
0.2
0
Absorbance
220
240
260
280
300
Wavelength (m)
1
2
3
4

Figure I-5

HCl solutions a brief search was undertaken to find a solvent which might have a sufficiently favorable distribution ratio and which could be used in future investigations. The solvents were chosen on the analogy of other elements which also showed a small distribution ratio between isopropyl ether and aqueous HCl.

β,β'-dichlorodiethyl ether was tested as it is a good extracting agent for arsenic (III) from HCl solutions (14). Three volume formal HCl was used as the medium. The distribution ratio was measured as 0.017, almost the same value as in isopropyl ether.

Benzene was found by Ramette to extract SbI_3 from HI solutions with distribution ratios greater than 2000 (15). On the possibility that $SbCl_3$ might behave in a similar manner experiments using benzene were carried out. The media used as the aqueous phases are given below in Table VII.

Table VII

Distribution Ratios Between Acid Solutions and Benzene

Antimony (III) = 0.075 VF

Aqueous phase	Distribution ratio $D = \frac{C_{Sb_{benzene}}}{C_{Sb_a}}$
2VF HCl	0.013
5VF HCl	0.02
1VF HCl-4VF $HClO_4$	0.069
0.4VF HCl-4.6VF $HClO_4$	0.115
1VF HCl-2VF H_2SO_4	0.01

Benzene is no better solvent than isopropyl ether. One anomaly appears. The distribution ratio is larger for 5VF HCl than for 2VF HCl in contrast to isopropyl ether and as shown below, other solvents.

On the basis of the analogy with mercury (II) which is poorly extracted by ethyl ether but is rather well extracted by ethyl acetate (16) the latter solvent was examined. From a 2VF HCl solution which was initially 0.025 F in antimony (III) the distribution ratio was 2.3 while from 5VF HCl the value was 1.2.

Other esters which have a lower solubility in water than ethyl acetate were tried. From 2VF HCl the distribution ratio into ethyl benzoate was 0.45. From 2VF HCl n-amyl acetate extracted antimony (III) to the extent of 46% or with a distribution ratio of 0.85.

As a quick check to see if the species of antimony (III) extracted by ethyl acetate was the same as that extracted by isopropyl ether a determination of n_{ester} was made. First the HCl solubility in the ester was measured since the correction of the chloride in the ester by the amount of HCl in the ester was necessary. For the material extracted from a solution 2VF in HCl and 0.0188 F in antimony (III) n_{ester} was determined to be 3.07 and the distribution ratio was 1.95. This value of n_{ester} is only approximate but it indicates that the main species extracted from 2VF HCl has a chloride to antimony ratio of 3 which is very much the same as in the case of isopropyl ether. The greater solubility of HCl in the ethyl acetate may account, at least partially, for the large distribution ratio. It would also allow more $HSbCl_4$ to dissolve in the organic phase as illustrated by the large value of n_e in isopropyl ether over 5VF HCl. There is some question about the validity of these latter experiments with ethyl acetate. Equilibrium in these systems was not attained as that would have meant that all of the ester would have been hydrolyzed.

The generalization that can be drawn from the experiments with the miscellaneous solvents is that the effectiveness in extraction of antimony (III) follows the solubility of the solvent in water or more exactly in HCl solutions. However, one further experiment was performed on the analogy of tartaric and citric acids with which antimony (III) forms well-known complexes. These are hydroxy acids which bond to the antimony both through the hydroxyl and carboxyl groups (17). Might not antimony (III) be extracted by a hydroxy compound which is insoluble in water? Such a compound appeared to be cyclohexanol. An experiment was performed with this solvent and the distribution ratio from 2VF HCl was found to be 3.9 the highest value encountered in this investigation. Cyclohexanol has the disadvantage as an extracting agent in that it is only slightly less dense than water; suspensions that form on shaking it with water require a long time to separate. This could be counteracted by the addition of some relatively inert solvent with a density appreciably less than that of water; an obvious choice would be isopropyl ether.

Two experiments were run with methyl n-amyl ketone, a solvent known for its extracting ability. From 6VF HCl, 0.25 F antimony (III) the distribution ratio was 0.71. From 2.9VF HCl, 0.08 F antimony (III) the distribution ratio was measured as 2.2.

VII. Discussion

In the first experiments carried out a stock solution 5.8VF in HCl and 0.85VF in antimony trichloride was diluted to give solutions that were 4 and 5VF in HCl. Values of n_e which exceeded four were unexpectedly obtained; the concentration of the antimony was possibly great enough that the activity coefficient of the HCl in such solutions was increased over that of pure HCl by the presence of the chloroantimonite ions. The amount of HCl in the ether would thereby be increased making the correction of C_{Cl_e} by HCl_e erroneous. This difficulty could be overcome by making the antimony (III) concentration small compared to that of the HCl. If the effect were real the value of n_e should be closer to four. On the contrary the experiments showed that the value of n_e increased considerably. The experimental value of 4.7 indicates the presence in the ether phase of a penta- or hexachloro species of antimony (III). Since the distribution ratio decreased with decreasing antimony (III) concentration polymerization of the species having an n_e of four was indicated. For the following reaction in 5VF HCl

$$SbCl_4^- + H^+Cl^- = HSbCl_5^- \qquad (24)$$

the relative amounts of the two antimony species is independent of the total antimony concentration and thus n_e would also be independent. If there is a dimer the reaction is

$$2\ SbCl_4^- + H^+ + 2Cl^- = HSb_2Cl_9^- \qquad (25)$$

and the relative amounts of $HSb_2Cl_9^-$ and $SbCl_4^-$ depend on the total antimony concentration in the aqueous phase and this is reflected in the change in n_e.

At lower acid concentrations the value of n_e is close to three, the conclusion being that the main extracted specis has three chlorides per antimony. The other extracted species must have two and four chlorides per antimony in order to produce values of n_e above and below three. These species were taken as $SbCl_2OH$ and $HSbCl_4$. The assumption was then made that $HSbCl_4$ was unionized in the ether phase but was completely ionized in the aqueous phase. If the assumption is not made no calculations can be carried out as the required data are unavailable. However, the relative constancy of K_{3-4} shows that this assumption was not unreasonable.

The spectrophotometric evidence indicates that in the aqueous phase a hydrate of $SbCl_3$ may exist. Figures I-3 and I-4 show that the absorption curves are quite different for the ether and aqueous solutions of the same antimony formality. The ether solution formed by the extraction from 2VF HCl has a much greater absorption at 230 mμ than the HCl solution itself. In 2VF HCl it is calculated that 29% of the antimony (III) is present as $SbCl_3$ and in the ether phase 87% of the antimony (III) is present as a trichloroantimony species. However, the absorbance at 230 m in the ether is five times the absorbance in the acid. Since the species of antimony with bonds to oxygen have their maximum absorption at smaller wavelengths than those without such bonds (2) it may be concluded that $SbCl_3(OH_2)$ exists in the aqueous phase while $SbCl_3$ exists in the ether phase. The calculated distribution ratio for $SbCl_3$, D_3, is therefore only a pseudoconstant and is actually equal to $K_{3h} \frac{D_3'}{a_{H_2O}}$ where D_3' is the distribution ratio for the species $SbCl_3$ and

$$K_{3h} = \frac{\left[SbCl_3(OH_2)\right]}{\left[SbCl_3\right] a_{H_2O}} \qquad (26)$$

Since a_{H_2O} does not change by very much in solutions that are 2-4VF in HCl the value of the distribution ratio calculated for the trichloro species should be approximately constant and no great inaccuracies are introduced.

VIII. Evidence of antimony (III) species from other sources

It is desirable at this point to look at the agreement of the results of the present investigation with other observations that have a bearing on the species of antimony (III) in HCl solutions. In the literature there can be found several types of information that provide support for the conclusions of the distribution study. Discussed below are double salt compounds of $SbCl_3$ with chlorides, the potential of the Sb (III)-Sb (V) half-cell in HCl solutions, the solubility of $Sb_4O_5Cl_2$ in HCl, the catalytic effect of antimony (III) on the hydrolysis of $SbCl_6^-$, spectrophotometric measurements, anion exchange of antimony (III) in HCl solutions, and the crystal structure of $(NH_4)_2SbCl_5$.

a. Double salts

Many double salts exist between $SbCl_3$ and the alkali and alkaline earth chlorides. There are two of the form $MCl \cdot SbCl_3$ where M is Na or Rb and many more in which there are five chlorides per antimony : Li, K, Rb, and NH_4 among the alkali group and Be, Ca, Mg, and Ba in the alkaline earth group (18). Only one compound, Tl_3SbCl_6, is known with six chlorides per antimony (19). The third common formula is $3MCl \cdot 2SbCl_3$ which has a chloride to antimony ratio of 4.5.

b. Crystal structure of $(NH_4)_2SbCl_5$

The existence of the above double salts does not prove the independent existence of discrete chloroantimonite ions. In $(NH_4)_2SbCl_5$ whose structure has been determined by Edstrand, Inge, and Ingri (20) there are individual $SbCl_5^{=}$ ions. These ions contain four Sb-Cl bonds of 2.62A and one of 2.36A opposite the unshared pair of electrons.

The crystal structure of $(NH_4)_2SbBr_6$ (21) which is a compound of so-called antimony (IV) have been determined. Each antimony is surrounded octahedrally by six bromides. The antimony in the corresponding Rb_2SbCl_6 is actually a mixture of antimony (III) and antimony (V) since it is diamagnetic rather than paramagnetic as would be required for antimony in the +4 oxidation state (22). The conclusion is that the hexacoordination of antimony (III) is stabilized by resonance with antimony (V).

c. Solubility measurements.

The solubility of $Sb_4O_5Cl_2$ in HCl has been measured by Lea and Wood (23). It would have been desirable to compare its solubility in $HClO_4$ but the solid exists only in equilibrium with HCl and conversely

Sb_2O_3 exists in equilibrium with $HClO_4$ solutions but not with HCl. The following equations may be written to show the reactions taking place on dissolving $Sb_4O_5Cl_2$ in HCl to produce the species found in 2VF HCl by the distribution study

$$Sb_4O_5Cl_2(s) + 6H^+ + 6Cl^- = 4SbCl_2OH + H_2O \qquad (27)$$

$$Sb_4O_5Cl_2(s) + 6H^+ + 10Cl^- = 4SbCl_3 + H_2O \qquad (28)$$

$$Sb_4O_5Cl_2(s) + 10H^+ + 14Cl^- = 4SbCl_4^- + H_2O \qquad (29)$$

Table VIII gives the solubility of antimony (III) in HCl. The concentration of HCl is approximated by $C_{Cl}-3C_{Sb}$.

Table VIII

Solubility of $Sb_4O_5Cl_2$ in HCl

HCl F	Sb (III) F	log a_{HCl}	log C_{Sb}+2
1.52	0.0116	0.140	0.066
1.68	0.0194	0.200	0.288
1.81	0.0299	0.237	0.477
1.94	0.0522	0.282	0.718
2.05	0.0755	0.321	0.879

From reaction 27 the slope of log C_{Sb} versus log a_{HCl} should be three, from reaction 28, five, and from reaction 29, six. The observed values are between 3.7 and 5.5 with an average of 4.6. The value of the slope to be expected was calculated by using the concentrations as found in the 2.18M HCl by the distribution measurements. It was found to be 4.7 which is very good agreement with the observed value given above.

d. Hydrolysis kinetics of $SbCl_6^-$

Neumann and Ramette (5) found that antimony (III) catalyzed the hydrolysis of $SbCl_6^-$ to $SbCl_5OH^-$. Since the catalytic effect of antimony (III) decreased with increasing HCl concentration they suggested that $SbCl_3$ was the species responsible and that increasing the HCl formed $SbCl_4^-$ which was inactive.

They measured the rate constant as a function of antimony (III) concentration in 2.2F HCl and found that the rate constant in that solution was given by the equation

$$k_0 = 7.75\ C_{Sb\ (III)}\ \text{minutes}^{-1} \qquad (30)$$

The rate of hydrolysis was measured in other concentrations of HCl with a constant concentration of antimony (III) = 0.385M. At this concentration $k_0 = 0.298\ \text{min}^{-1}$. Table IX gives the observed rate constant as a function of the HCl concentration and the value of k/k_0.

Table IX

Rate Constant of Hydrolysis of $SbCl_6^-$ in HCl

HCl F	$k \times 10^3\ \text{min}^{-1}$	k/k_0
6.17	1.2	0.004
5.35	7.4	0.025
4.55	25	0.084
3.51	83	0.278
2.63	217	0.738

The value of k/k_0 reflects the concentration of the catalytically active species. If $SbCl_3$ were the active species the value of k/k_0 in 2.63F HCl would be about 0.96 since there is little change in the concentration of $SbCl_3$ in the interval 2.2 to 2.6 F HCl as found in the distribution study. In 3.5 F HCl the concentration of $SbCl_3$ is about 70% of its value in 2.2 F HCl. The drop in the $SbCl_3$ concentration is not sufficient to account for the decrease in the relative rate constant.

On the other hand if $SbCl_2OH$ is the active species a closer relationship is observed. Table X gives the ratio of the concentration of $SbCl_2OH$ in HCl solutions relative to its concentration in 2.2 F HCl. The ratios were calculated from the values given in Table VI.

Table X

Relative Concentrations of $SbCl_2OH$ in HCl Solutions

HCl F	% $SbCl_2OH$	% $SbCl_2OH$ / % $SbCl_2OH$ in 2.2 F HCl
2.2	33.6	....
2.6	21	0.54
3.5	5	0.13
4.5	1/2	0.02

The agreement is not very good but the trend is quite similar.

e. Spectrophotometric measurements.

The fact that no peak was observed in the spectrum of $SbCl_3$ in 1-4VF HCl (Figure I-3) while Whitney and Davidson (6) and Desesa and Rogers (24) found a peak at 230 mμ in 11.5 and 6.7F HCl solutions may be interpreted as their having observed the spectrum of a more chlorinated species than the $SbCl_4^-$ as they assumed. From Neumann's investigation of the antimony (V) species in HCl (2) the shift in the position of the absorption peak for the hydrolyzed species was -20 mμ per hydrolysis. If the same value is valid for antimony (III) chloride complexes then the peak for $SbCl_4^-$ is approximately at 210 mμ, just at the edge of the observable range if Whitney and Davidson were observing the spectrum of $HSbCl_5^-$. It is noted that as the HCl concentration was increased the absorption at 220mμ increased indicating the movement of a peak toward the range of the spectrometer.

f. Anion exchange

Kraus and Nelson (25) as a part of their survey of the anion exchange of many elements looked at antimony (III) in HCl solutions. Their published graph of log D versus C_{HCl} is quite small and cannot be used for quantitative calculations. However, the resemblance of the curve to the distribution ratio curve in Figure I-2 is unmistakeable. It has a peak at

2 F HCl and gradually declines with increasing HCl concentration. Their derivation by slope analysis of the species present requires that the average charge on the antimony be zero at this point meaning that n_a is three. This agrees exactly with the results of the present investigation.

That the maximum absorption in anion exchange should occur at the point where the average species is the neutral molecule is conceptually odd if one considers that it is the anion which is supposedly being exchanged. However, the absorption of the neutral molecule is completely equivalent to the exchange of a singly charged anion. The expressions for the two viewpoints are given in reactions 31 and 32 where R^+ is the resin and X^- is the anion of the supporting electrolyte.

$$R^+X^- + MX_3 = R^+ MX_4^- \qquad (31)$$

$$R^+X^- + MX_4^- = R^+ MX_4^- + X^- \qquad (32)$$

The equilibrium constant for the above reactions differ only by the constant for the formation of MX_4^- from MX_3. Phenomenologically the first equation states that the distribution of the metal M should decrease with increasing X^- concentration because MX_3 is converted to non-absorbable MX_4^-; the second equation says that the absorption decreases with increasing X^- concentration by a direct consequence of the equilibrium.

g. Potentiometric studies

The potential of the antimony (III) - antimony (V) half cell as measured by Brown and Swift is -0.6716v in 2VF HCl, -0.7456v in 3.5VF HCl, and -0.7836v in 4.5VF HCl versus the normal hydrogen electrode (3). They suggested that the actual electrode reaction was

$$SbCl_4^- + 2Cl^- = SbCl_6^- + 2e^- \qquad (33)$$

When antimony (III) is oxidized to the +5 oxidation state by chlorine in 3.5VF HCl a yellow color is formed which disappears in time. Neumann found that it is $SbCl_6^-$ which gives rise to this color and that on being formed it slowly hydrolyzes to $SbCl_x(OH)_{6-x}^-$ where x depends on the equilibrium HCl concentration. Now

$$E = E_0 - \frac{0.059}{2} \log \frac{[SbCl_6^-]}{[SbCl_4^-][Cl^-]^2} \qquad (34)$$

but

$$[SbCl_6^-] = \frac{K[SbCl_x(OH)_{6-x}^-]a_{HCl}^{2x}}{a_{H_2O}^{x}} \qquad (35)$$

The change in E in going from 2VF to 3.5VF HCl is a consequence of the change in the concentrations of $SbCl_4^-$ and $SbCl_6^-$. From the present study $[SbCl_4^-]$ is known but $[SbCl_6^-]$ must be estimated. It will be assumed that the antimony (V) species is the same in both 2VF and 3.5VF HCl. The value of $[SbCl_6^-]$ from equation 35 is substituted into equation 34.

E_1 = E in 3.5VF HCl

E_2 = E in 2VF HCl

$$\Delta E = E_2 - E_1 = \frac{0.059}{2} \log \frac{[SbCl_x(OH)_{6-x}^-]_{(2)}\,[SbCl_4^-]_{(1)}\,a_{HCl\,(1)}^{2x-2}\,a_{H_2O\,(2)}^{x}}{[SbCl_x(OH)_{6-x}^-]_{(1)}\,[SbCl_4^-]_{(2)}\,a_{HCl\,(2)}^{2x-2}\,a_{H_2O\,(1)}^{x}} \qquad (36)$$

Although it is not known exactly what the value of x is it is reasonable to take it to be 3 or 4 on the basis of the data given by Neumann (2). Setting the $SbCl_x(OH)_{6-x}^-$ concentrations equal and substituting the proper activities of HCl and H_2O and the concentrations of $SbCl_4^-$ the value of ΔE was computed. It was assumed that the activity coefficients of the antimony species were equal. For $x = 3$ $\Delta E = -0.042$v and for $x = 4$ $\Delta E = -0.065$v. The observed value was -0.064v. This is only approximate by the result does indicate that the values for the $SbCl_4^-$ concentrations are not unreasonable.

IX. Summary

The distribution of tripositive antimony between isopropyl ether and HCl, HCl-$HClO_4$, and HCl-NaCl solutions has been investigated. The concentrations of the antimony (III) and the chloride in the ether phase have been measured as a function of the aqueous phase. On the basis of the values for the average number of chlorides and hydrogens per antimony as derived from the relationship of the distribution ratio and the aqueous HCl activity a model of the antimony (III) species was constructed. The model had the species $SbCl_2OH$, $SbCl_3$, $SbCl_4^-$, and $HSbCl_5^-$ in the aqueous phase and $SbCl_2OH$, $SbCl_3$, and $HSbCl_4$ in the ether phase. The following constants were calculated by use of this model.

$$K_{2-3} = \frac{[SbCl_3]_a \ a_{H_2O}}{[SbCl_2OH]_a \ a^2_{HCl}} = 0.145$$

$$K_{3-4} = \frac{[SbCl_4^-]_a}{[SbCl_3]_a \ a_{HCl}} = 0.34$$

$$D_2 = [SbCl_2OH]_e / [SbCl_2OH]_a = 0.0080$$

$$D_3 = [SbCl_3]_e / [SbCl_3]_a = 0.062$$

The fraction of antimony (III) present in 2 M HCl as $SbCl_4^-$ was found to be 0.38 while in 3 and 4 F HCl the proportion increased to 0.65. The fraction of antimony present as $SbCl_3$ decreased from 0.28 to 0.15 as the HCl concentration was raised from 2 to 4 M. The fraction of $SbCl_2OH$ in the same range of HCl went from 0.34 to 0.02. Evidence was found for large amounts of $HSbCl_5^-$ and perhaps $H_2SbCl_6^-$ in 5 F HCl.

The model was found to be consistent with the known solubility of $Sb_4O_5Cl_2$ in HCl. The model is supported by reasonable agreement with evidence from spectrophotometric experiments, measurements of the potential of the Sb (III)-Sb(V) half-cell, and antimony (III) catalyzed hydrolysis of $SbCl_6^-$ as found by other investigators.

Some spectrophotometric studies were made of antimony (III) in HCl and isopropyl ether solutions. No peak for an antimony species was observed. The greater absorption of ether solutions in contrast to the HCl solutions of the same antimony (III) concentration was construed to indicate the presence of a hydrated $SbCl_3$ in the aqueous phase.

A brief study of the distribution of antimony (III) between HCl solutions and various solvents was made. Cyclohexanol and methyl n-amyl ketone of those investigated were found to be the best extractants.

PART II

THE INFRARED SPECTRA AND PROBABLE STRUCTURES OF SOME NITROGEN-SULFUR COMPOUNDS

THE INFRARED SPECTRA AND PROBABLE STRUCTURES OF SOME NITROGEN-SULFUR COMPOUNDS

I. Introduction.

Originally this investigation was intended to study the infrared spectrum of N_2O_3 as a continuing part of the studies at this laboratory but it was found that several other laboratories were well advanced in the study of this problem. Any work started at that time would not have been completed before these other laboratories had obtained their results. In a literature search on compounds related to the nitrogen oxides there were found several references to nitrogen sulfur compounds. It was decided to reinvestigate the infrared spectra of N_4S_4 and $N_4S_4H_4$ in view of the actual structures of the molecules which were not known to the original investigators. These compounds were examined and it was found that the previously observed spectrum of N_4S_4 was correct but there were several differences between the published spectrum of $N_4S_4H_4$ and the spectrum as determined here.

In the literature search mentioned earlier, the compounds of nitrogen-sulfur, and fluorine synthesized by Glemser were found. Since he indicated that most of the new compounds were gases an attempt to determine their structures by infrared spectroscopy was felt to be profitable. The only previous infrared studies of compounds containing nitrogen-sulfur bonds were those of N_4S_4 and $N_4S_4H_4$ and of sulfamic acid. Also Glemser's compounds were expected to have N-S double bonds and these had never been observed before by infrared methods.

Glemser had characterized his new compounds by the classical methods of chemical analysis and determination of molecular weights. No attempt was made to utilize modern physical methods to identify and characterize these new compounds. Moreover there were some inconsistencies in his results, for all of the compounds that he claimed to have made yielded $SO_3^{=}$, NH_4^+, and F^- on hydrolysis by strong base, despite the presumed existence of different formal oxidation states of the sulfur in the different compounds, SN_2F_2, SNF, NSF, and NSF_3.

One study of the infrared spectrum of the product of the reaction between N_4S_4 and AgF_2, as reported by Glemser, was carried out by Gallup and Koenig. Their assignments of frequencies to what they thought was SNF were quite unreasonable.

It was in order to explain these contradictions and to elucidate the molecular structure of these new compounds that the present study was initiated.

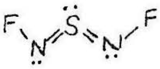
II. Previous work on the nitrogen-sulfur-fluorine compounds.

In 1955 Glemser and his co-workers synthesized the first nitrogen-sulfur-fluorine compound, $N_4S_4F_4$, by fluorination of N_4S_4. He stirred a suspension of AgF_2 in a solution of N_4S_4 in CCl_4 which was held at the boiling point under reflux for 15 minutes. The compound was recovered by recrystallization from benzene.

If instead of stopping the heating after 15 minutes he continued the refluxing for two hours and condensed the gas produced in a trap at dry ice-acetone temperature (-80°C) he obtained a mixture of compounds which he fractionally distilled under reduced pressure. The main product he believed at that time to have the formula SN_2F_2 (26). He also found at times that there was another gaseous nitrogen-sulfur-fluorine compound which he was unable to separate completely by fractional distillation from the supposed SN_2F_2. The compound was unstable, reacting with SN_2F_2 to form a solid, $S_3N_2F_2$, which condensed on the walls of the container

(26, 27). After allowing a sufficient time to pass for all of the unstable compound to react he claimed to have obtained pure SN_2F_2.

Glemser measured the molecular weight by vapor density measurements and the fluorine and sulfur contents of several mixtures believed to contain SN_2F_2 and the unknown compound. The values he obtained for these quantities are not sufficient to derive the formula of the unknown compound. He assumed that the compound was SNF since the average molecular weight of the mixtures was less than that of SN_2F_2, meaning that the compound had a smaller molecular weight than the smallest one he measured which was 70. On this basis he calculated the sulfur and fluorine contents of the mixtures and found the agreement with the experimental values to be excellent.

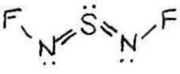
Glemser assigned the formulae to the various compounds on the basis of molecular weights, determined percentage composition (sulfur and fluorine), and the products of alkaline hydrolysis. For example, in the case of SN_2F_2 he said that the products of the alkaline hydrolysis were $SO_3^{=}$, NH_4^+, (perhaps NH_3) and F^-, indicating that the sulfur is in the +4 oxidation state. The structural formula he says is therefore .
Unfortunately he ignores the fact that a balanced equation cannot be written which yields only the above mentioned products. The implication is that the material he assumes to be a pure compound may be a mixture.

The hydrolysis of a mixture of SNF and SN_2F_2 believed to contain a high percentage of SNF produced $SO_3^{=}$, $S^{=}$, NH_4^+, and F^-. He did no analyses to determine the proportion of each product so that no definite idea of the true reaction can be formed.

Glemser claimed to have prepared two additional compounds containing the three elements. He pyrolyzed SN_2F_2 at 300mm pressure in a quartz tube at 250°C for 24 hours to synthesize NSF with SiF_4 and N_2 as detected byproducts (28). Another method of producing the same compound was to allow SN_2F_2 to boil under reflux for six days. This latter process also made NSF_3 and an unknown compound of higher boiling point (28). NSF_3 can also be prepared by passing SNF or SN_2F_2 over AgF_2 at room temperature (29).

In all his syntheses Glemser is very brief and gives few details of experimental conditions. Particularly lacking are any details of the purification processes and any attempts to characterize the products by modern methods.

The physical properties of the various compounds as reported by Glemser are given in Table I. Table II consists of the physical properties of possible impurities that might have been found as byproducts of the different syntheses.

Until very recently only one attempt at a complete study of the infrared spectra of any of these compounds has been published since they are so new. This was by Gallup and Koenig (49). They indicated that they had prepared SN_2F_2 by the method of Glemser but they gave no details and did not report whether they tried any purification of the reaction product. Using the model of the structure proposed by Glemser  they assumed that the molecule had C_{2v} symmetry although there is no obvious requirement that this be true. The symmetry might equally well be C_s or C_2 depending on the relative orientation of the fluorines.

The spectrum reported by Gallup and Koenig is reproduced in Figure II-1. They assigned the bands found at 754, 725, and 508 cm^{-1} to A_1 frequencies with the fourth A_1 frequency calculated from combination bands as 70 cm^{-1}. The bands at 805, 623, and 421 cm^{-1} were taken to be the B_1 frequencies. Their assignment of the lowest A_1 frequency was based on the N-S-N angle bending frequency in N_4S_4 (50). The other assignments were made on the basis of the shapes of the band envelopes

Table I

Physical Properties of Nitrogen-Sulfur-Fluorine Compounds.

	State and color	Melting point (°C)	Boiling point (°C)	Heat of vaporization (kcal/mole)	Ref.
SN_2F_2	colorless gas	-108	-11	5.30	26
SNF	" "	- 80	0	-	26
NSF	" "	- 79	4.8	5.30	28
NSF_3	" "	- 79	-23	5.21	29

Table II

Physical Constants of Possible Impurities.

Compound	Melting Point(°C)	Boiling Point(°C)	Heat of vaporization (kcal/mole)	Reference
CCl_4	-23	76.8	7.15	30
$CFCl_3$	-111	24.1	-	31
CF_2Cl_2	-160	-28	-	31
CF_3Cl	-181	-80	-	31
CF_4	-184	-128	2.947	32
COF_2	-114	-83.1	-	33
COS	-138	-50.2	-	34
N_2F_2 trans	-172	-111.4	3.40	35
cis	-195	-105.7	3.67	35
N_2F_4	-	-73	3.17	36
NF_3	-206.8	-129	2.87	37
NOF	-132.5	-60	4.54	38
OF_2	-224	-144.8	2.64	39
SF_4	-121	-40	6.32	40
SF_6	- 50	-63.7s(1)	-	41
S_2F_{10}	- 54	29	6.95	42
SOF_2	-130	-44	5.15	43
SOF_4	- 99	-49	5.09	44
SOF_6	- 86	-35.1	5.21	44
SO_2F_2	-136.7	-55.4	4.79	45
SO_2	- 75.46	-10.02	5.96	46
ClF	-155.6	-100.1	4.80	47
ClF_3	- 82.6	11.9	6.58	47
SiF_4	- 90	-95.3	-	48

(1) s= sublimes

Figure II-1. Spectrum of product obtained by Gallup and Koenig (49)

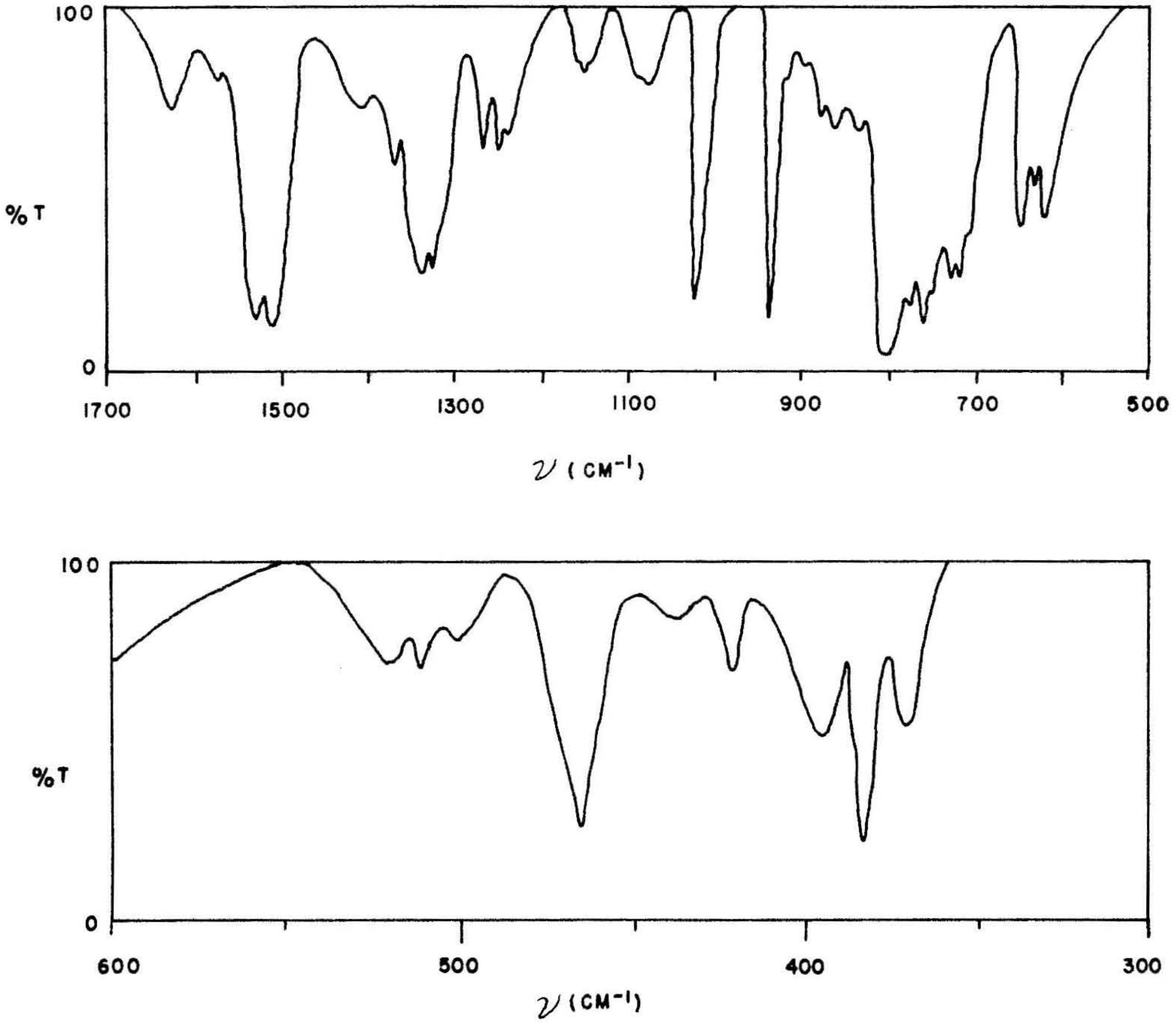

100
%T
0
1700
1500
1300
1100
900
700
500
ν (CM^{-1})
100
%T
0
600
500
400
300
ν (CM^{-1})

FIGURE II-1

and the band intensities. Their observed frequencies are reproduced below in Table III.

They believed that they had also observed the spectrum of SNF because there were three bands in their spectrum at 1024, 941, and 390 cm^{-1} which decreased with the passage of time. They said that the lowest frequency corresponded to the angle bending mode, the other two to the bond stretching modes. These tentative assignments did not seem reasonable even to Gallup and Koenig and as will be pointed out below their doubts were entirely justified. Included in Table III are the assignments which are based on the results of the present investigation.

From the appearance of their published spectrum it seems difficult to see how the band shapes of the 754, 845, 864, and 884 cm^{-1} bands can be precisely determined. Since there appears to have been no attempt at purification of their product it is apparent that Gallup and Koenig did not consider the possibility of impurities which could have given rise to some of the observed bands. On the basis of the information found in the present work Gallup and Koenig's assignments were found to be fallacious.

Glemser, Richert, and Haeseler have taken the infrared spectra of two nitrogen-sulfur-fluorine compounds. They reported a study of the BF_3 adduct with NSF_3 but neither the spectrum nor any details of the spectrum were given (51). The other study gave a spectrum of SNF (52) which is reproduced in Figure II-2. They claimed that the sample was of very high purity. The figure shows a complete band at 1380 cm^{-1} and part of another which is cut off at 650 cm^{-1}. All that can be deduced is that the latter band is more intense than the one at 1380 cm^{-1}. The 1380 cm^{-1} band has a double peak which seems very unlikely for an asymmetric triatomic molecule since the high frequency

Table III

Infrared Bands and Assignments of Gallup and Koenig's Product.

Band (cm^{-1})	Assignment (G and K)	Assignment from information found in present investigation
1625	$2\nu_6$ (A_1)	B
1525	$\nu_2 + \nu_6$ (B_1)	B
1405 (1)	$\nu_2 + \nu_4 + \nu_7$ (B_1)	
1330	$\nu_2 + \nu_7$ (B_1)	D, SOF_2
1251	$2\nu_7$ (A_1)	C
1150	$\nu_2 + \nu_8$ (B_1)	D
1080	$\nu_2 + \nu_8 - \nu_4$ (B_1)	$CFCl_3$
883	$\nu_4 + \nu_6$ (B_1)	SF_4
864	?	SF_4
845	$2\nu_8$ (A_1)	$CFCl_3$
805	ν_6 (B_1)	B
754 (2)	ν_1 (A_1)	B
725	ν_2(A_1)	SF_4
623	ν_7(B_1)	A
508	ν_3(A_1)	
421	ν_8 (B_1)	
70 (calc.)	ν_4 (A_1)	

(1) Believed to be a window peak.

(2) Measured on their published spectrum (Fig. II-1) the 754 cm^{-1} band is actually at 775 cm^{-1}.

Figure II-2. Spectrum of SNF by Glemser, Richert and Rogowski (52)

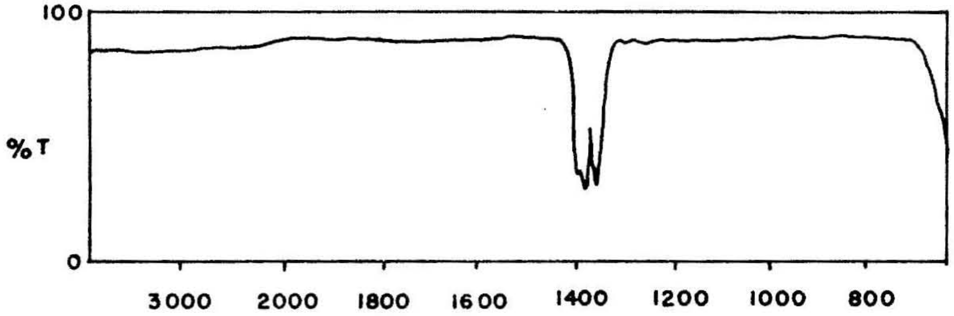


FIGURE II - 2

stretching modes should be of the A type with prominent Q branches. In the same note they report an electron diffraction study which yielded an N-S distance of 1.59 ± .05A, an N-F distance of 1.42 ± .05A and a bond angle of $120^\circ \pm 5^\circ$.

Glemser's earlier evidence on the identification and structure of the nitrogen-sulfur-fluorine compounds was based on the nature of the products of the hydrolysis in strongly basic solution. Since these hydrolysis reactions cannot be expressed by balanced equations there is no certainty that the structural relationships deduced are correct although the empirical formulae may be.

T. S. Piper has done some preliminary investigations of the nuclear magnetic resonance and the mass spectrum of NSF_3 (53). He concludes that all the fluorines are attached to sulfur since he finds that SF_3^+ is a prominant peak in the mass spectrum. This evidence indicates that the structure is actually $N{\equiv}SF_3$.

The synthesis of some organoiminosulfur difluorides, $RN{=}SF_2$, by reaction of SF_4 with inorganic cyanides, cyanates, thiocyanates and organic isocyanates has been reported recently (54). Only one comment was made on the infrared spectra of these compounds; namely that there is a band in the region 7.15-7.35μ which is believed to be characteristic of the N-S bond in these compounds.

Currently the microwave spectrum of NSF_3 is being investigated in several laboratories but no results have been published at this time (53, 55).

III. Preparation and fractionation of N-S-F compounds.

The syntheses in this investigation follow in general the procedures of Glemser and his co-workers (26, 28, 29). Several preparations were used because the product of the synthesis is unstable, turning red over a period of days, even when kept at -60°C or lower.

The N_4S_4 was prepared by passing NH_3 into a solution of 30g of technical S_2Cl_2 in 200 ml of technical grade chloroform in a 500ml flask according to the method of Arnold, Hugill, and Hutson (56). The reaction at first produces a yellow precipitate which later gradually turns to a dull brown. At the end of an hour, during which the flask is kept cool in an ice bath, the material in the flask consists of a dark red precipitate covered by a dark red solution. This mixture is allowed to stand at room temperature for a day to allow the precipitate to coagulate completely. This permits the various components of the mixture of solids to crystallize into large crystals, a necessity for the next step in the purification.

The $CHCl_3$ solution was decanted from the precipitate which was filtered and dried. The precipitate was then washed with water to remove the NH_4Cl. If this washing were done immediately after the synthesis an amorphous, gray-yellow, spongy mass resulted, rather than the mixture of crystals of sulfur and N_4S_4 obtained if the washing is delayed. The mixture was washed with CS_2 to dissolve the sulfur and leave the greater part of the N_4S_4. The final purification of the N_4S_4 was a recrystallization from benzene, which gave the product in the form of bright orange needles 2-5mm long.

The AgF_2 used in the following synthesis was a technical grade and was purchased from the Harshaw Chemical Company. It was a brown-black powder with some white lumps. After opening the original can the AgF_2 was divided into six parts which were placed in small polyethylene bottles so that other fresh material would be available if the AgF_2 in one container lost its effectiveness because of repeated openings and contact with air.

A quick determination of the oxidizing power of the AgF_2 was carried out by adding a weighed amount to a KI solution and titrating the iodine liberated with standard thiosulfate solution. The analysis showed that the material was 71% AgF_2 in terms of oxidizing power.

a. Preparation I.

The first attempt at preparing SN_2F_2 was made by placing 2.5g of N_4S_4 in 250ml of CCl_4 in a 500 ml three-necked flask and adding 1.5g of AgF_2 through one neck. That neck was closed with its stopper and a heating mantle was used to heat the CCl_4 to boiling while the CCl_4 vapor was condensed in a reflux condenser attached to the middle neck. Any SN_2F_2 or SNF which formed passed over into a trap which was cooled in a dry ice-acetone bath (-80°C). This apparatus is depicted in Figure II-3.

A series of color changes occurred as the reaction proceeded. On addition of the AgF_2 the light orange solution turned to a yellow-green. The latter color disappeared on heating and was replaced by a deep red. After two and a half hours of heating the red color had become noticeably lighter. This red color persisted as long as the CCl_4 was in contact with AgF_2. After the reaction was over and the CCl_4 had cooled the solution was decanted off into a bottle where the color faded after a day to an orange hue very similar to that of an N_4S_4 solution. In the bottle a white solid precipitated. This might be $N_4S_4F_4$, a possible product of the reaction.

The gaseous product of this reaction which condensed in the cold trap was a part white, part yellow solid. The cold trap was detached from the synthesis apparatus and attached to a vacuum system shown in Figure II-4. A gas cell 9cm long with KBr windows was filled in the manner described in the section on taking of spectra. The infrared

Figure II-3. Apparatus for synthesis and collection of gaseous nitrogen-sulfur-fluorine compounds

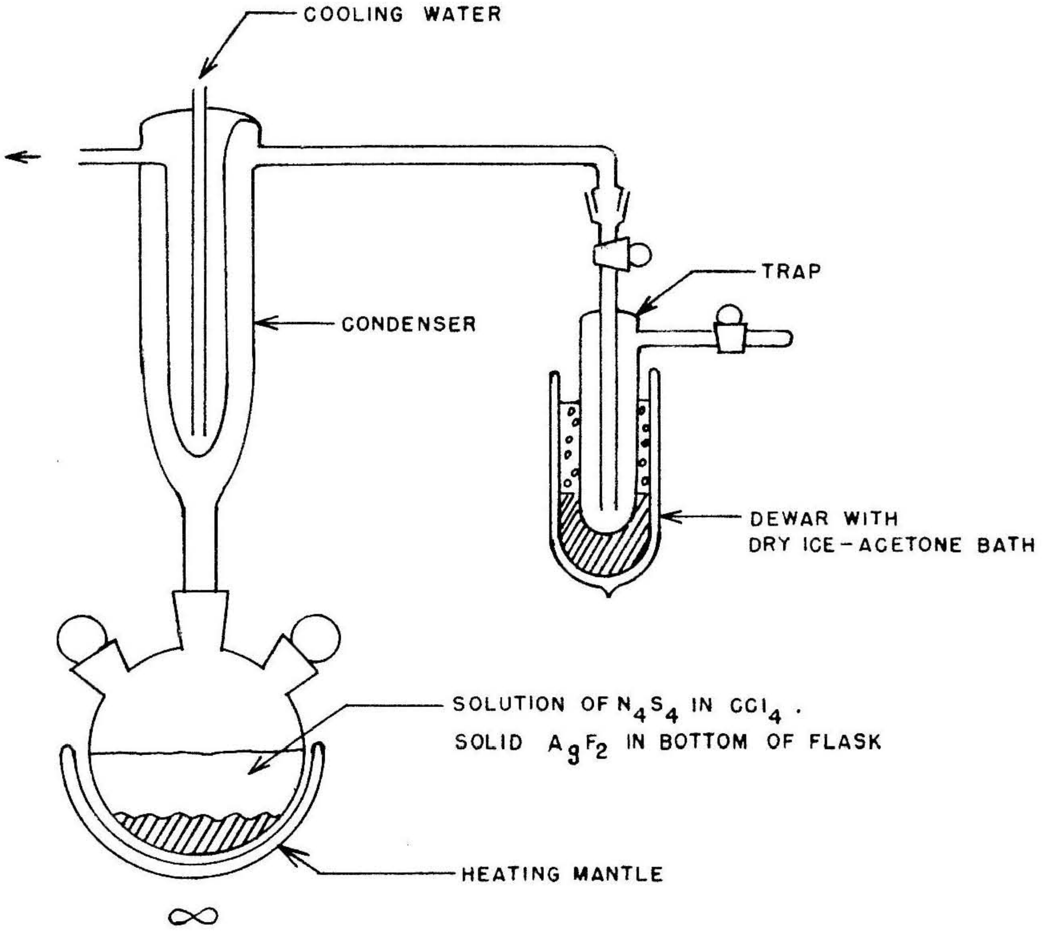
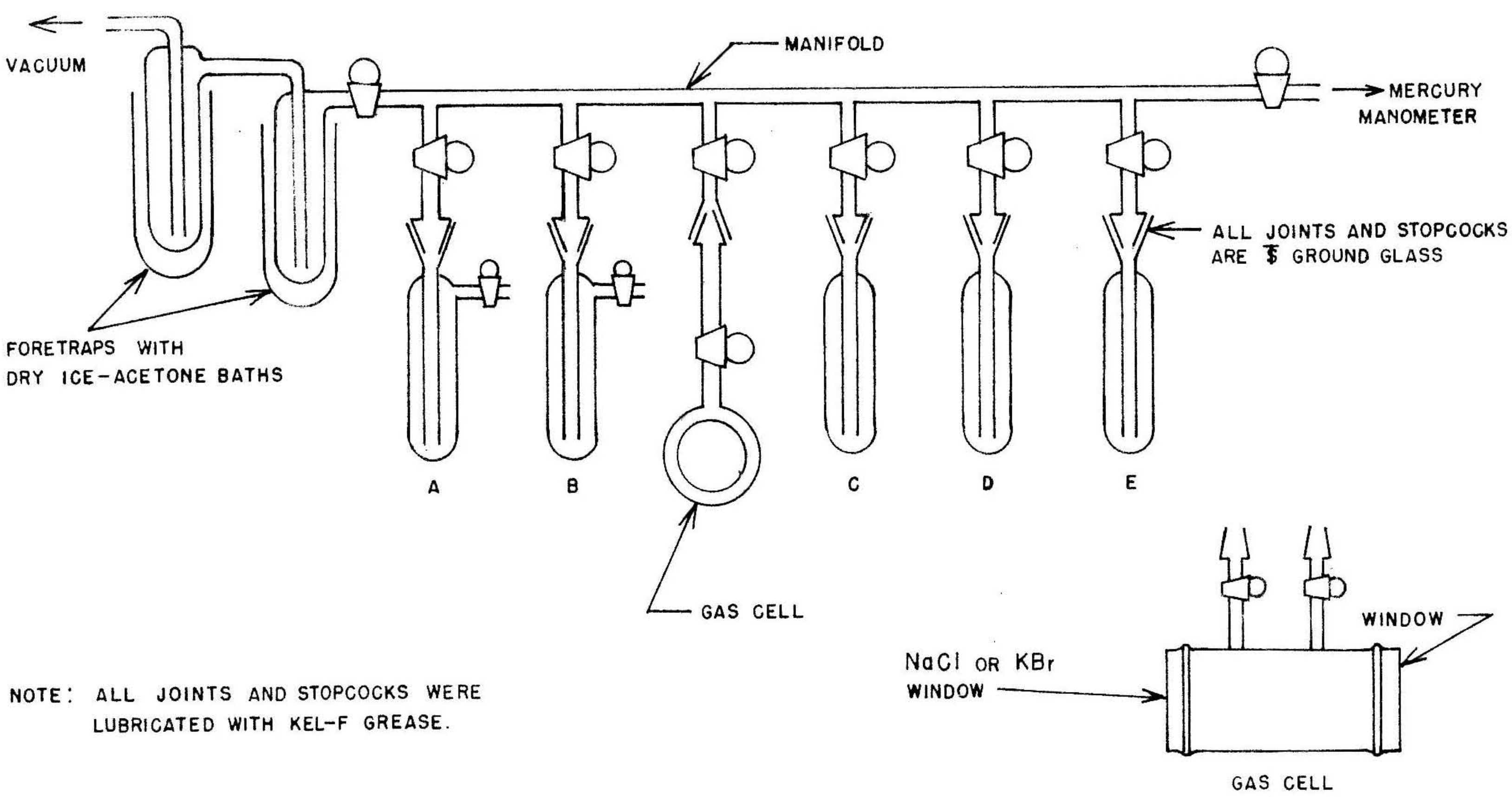

COOLING WATER
TRAP
CONDENSER
DEWAR WITH
DRY ICE-ACETONE BATH
SOLUTION OF N_4S_4 IN CCl_4.
SOLID AgF_2 IN BOTTOM OF FLASK
HEATING MANTLE

FIGURE II-3

Figure II-4. Vacuum system for distillation of product and filling of gas cell



NOTE: ALL JOINTS AND STOPCOCKS WERE LUBRICATED WITH KEL-F GREASE.

FIGURE II - 4

spectrum of the vapor of the product was taken on a Baird infrared spectrometer, Model B. The spectrum is shown in Plate I. The bands at 795 and 775 cm^{-1} are those of CCl_4 (57). The compounds which produced the bands at 1360 and 850 cm^{-1} were unidentified at this time. The absence of any of the bands reported by Gallup and Koenig indicated that the synthesis had produced none of the desired N-S-F compounds. The material in the cold trap appeared to be mainly CCl_4 which must have passed through the condenser.

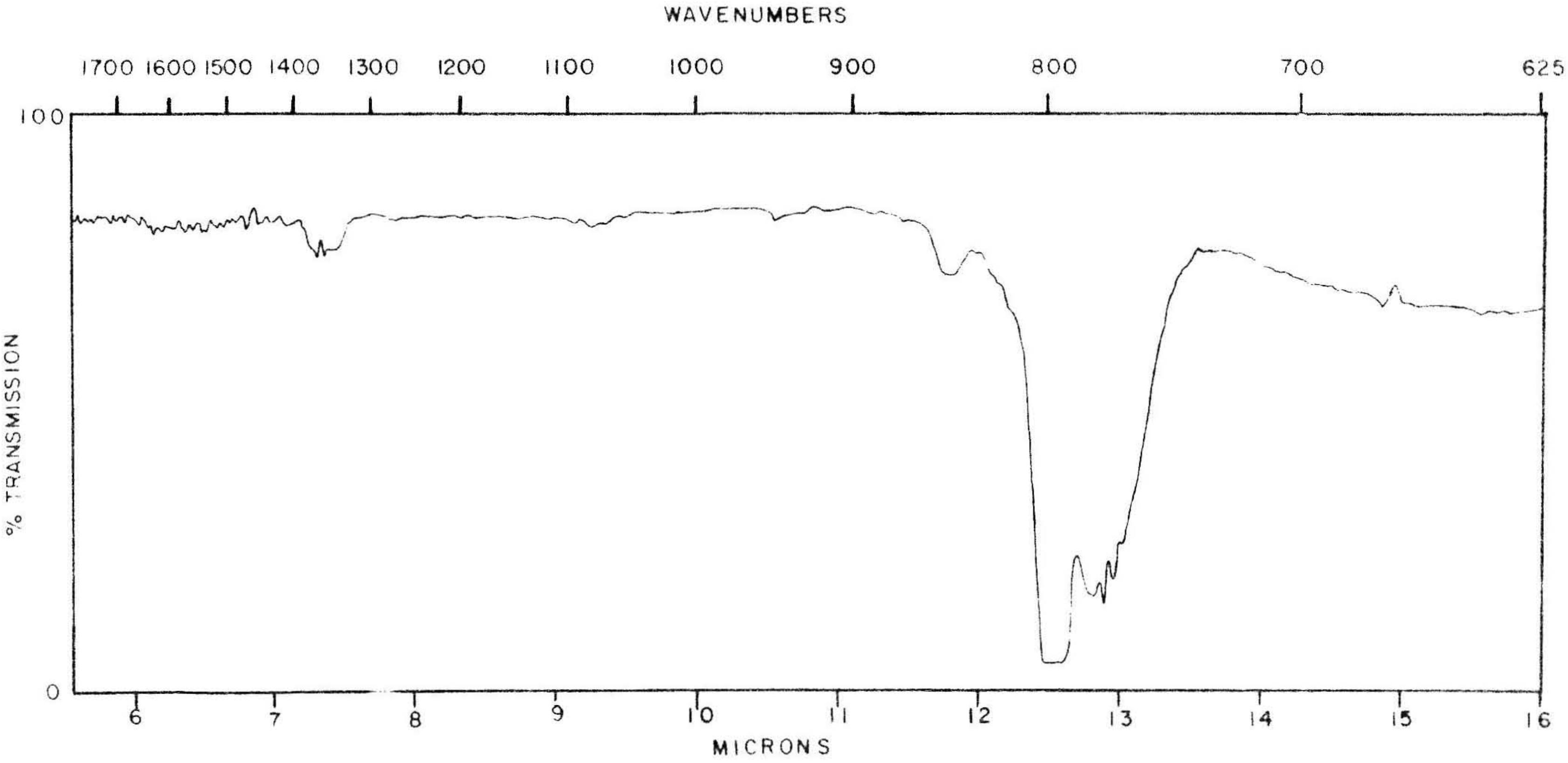
On the assumption that the amount of AgF_2 used had been inadequate an additional 5g of it were added to the CCl_4 solution and the mixture was heated for an hour. A red liquid was observed to condense in the cold trap. The spectrum of the vapor of the red liquid was obtained and is shown in Plate II.

In Plate II the bands of $CFCl_3$, SO_2, and SiF_4 were observed and were identified by means of the criteria given in section III. The bands of SO_2 were particularly intense indicating that there was oxygen present during the synthesis and that it combined with some sulfur from the N_4S_4. There were some new bands at 650, 1530, and 1630 cm^{-1} which were unidentified and were suspected to belong to new compounds. The broad absorption between 750 and 850 cm^{-1} was believed to be due to CCl_4. The new bands were much less intense than those of the impurities. To increase the yield of new compounds and to minimize the amount of impurities it was decided to adhere to Glemser's original conditions in the next synthesis but with some improvements suggested by a knowledge of the nature of the impurities.

b. Preparation II.

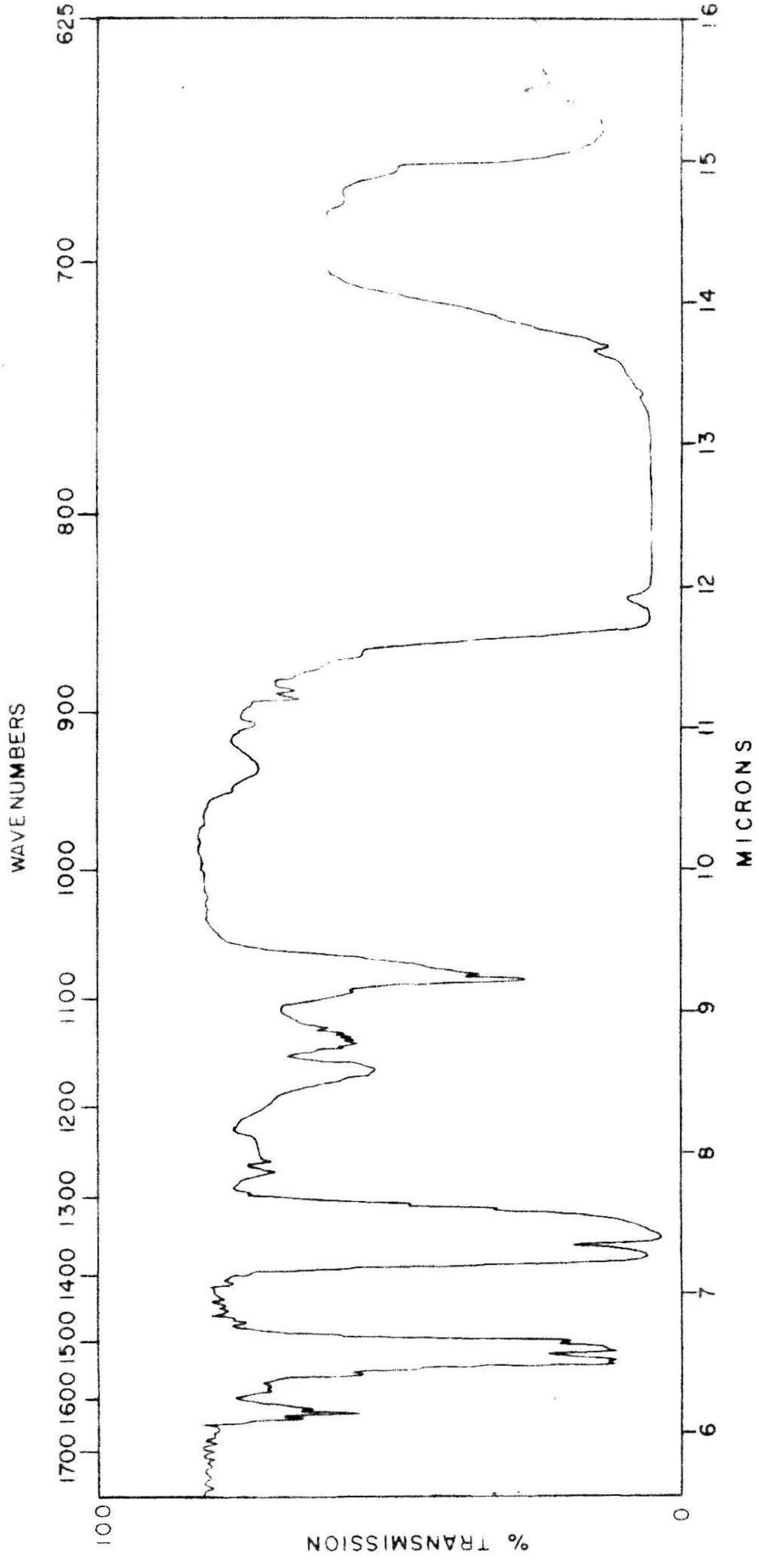
In an attempt to improve the yield of new compounds and decrease the amount of byproducts a second preparation was carried out under the

Plate I. Spectrum of product of preparation I (first heating)


WAVENUMBERS
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
625
100
% TRANSMISSION
0
6
7
8
9
10
11
12
13
14
15
16
MICRONS

(61)

Plate II. Spectrum of gas given off at -70°C from preparation I (second heating)


WAVE NUMBERS
625
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
MICRONS
16
15
14
13
12
11
10
9
8
7
6
% TRANSMISSION
100
0

following conditions.

1. The CCl_4 was freshly distilled from P_2O_5 in order to remove water.
2. The reaction mixture was stirred by a magnetic stirrer to keep the surface of the AgF_2 freshly exposed.
3. The condenser water was precooled in an ice bath to minimize the amount of CCl_4 that would get past the condenser.
4. Dry N_2 was bubbled through the N_4S_4 solution before the addition of AgF_2 in order to sweep out any oxygen that might have been present.
5. The reaction mixture was heated for seven hours to insure completeness of the reaction.

The yield from this preparation was a milliliter of a pink liquid in the cold trap. After three days at -80°C the color had deepened to a red.

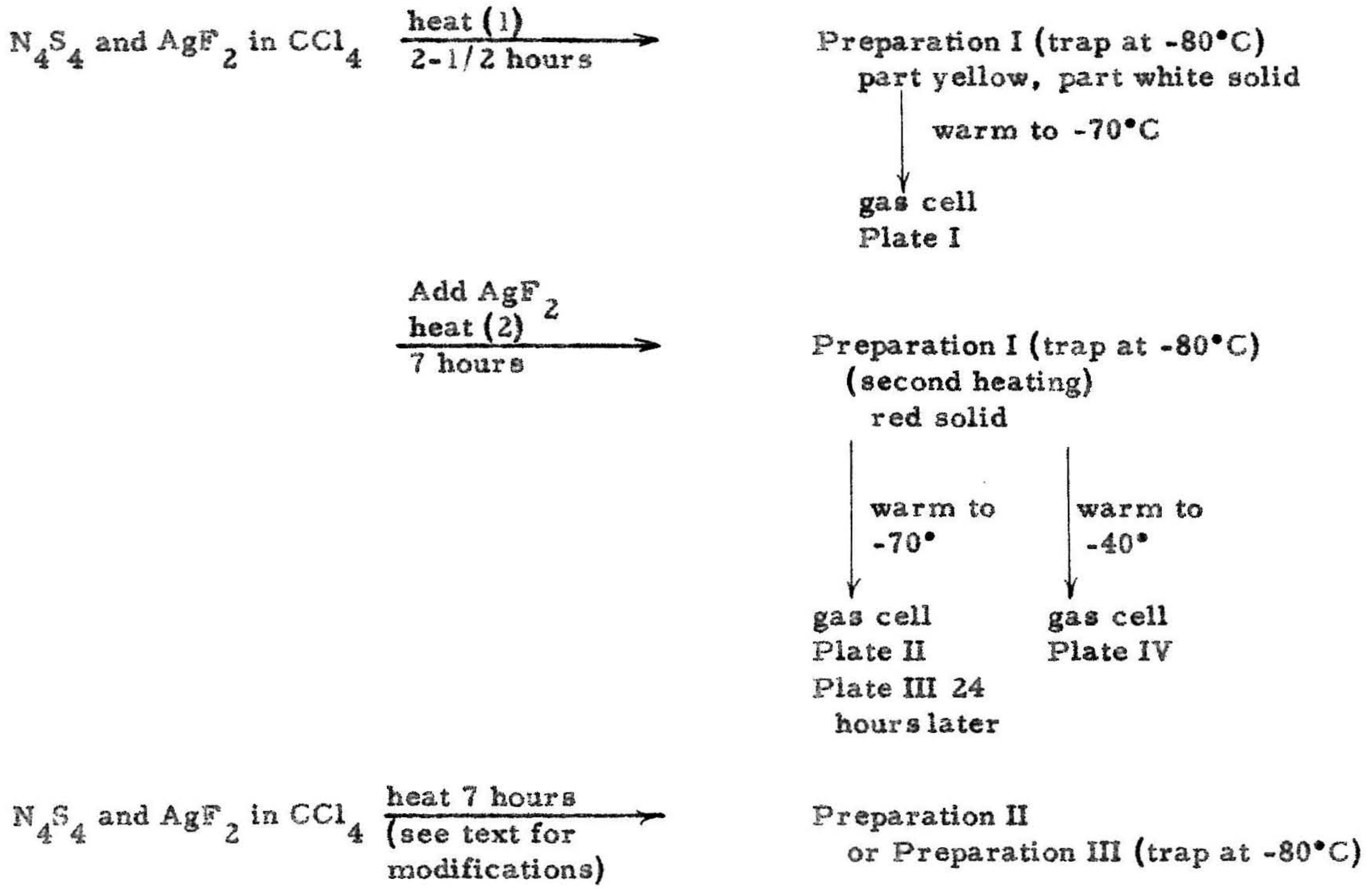
c. Preparation III.

Preparation III was a repetition of preparation II since the latter had turned into a red solid after a month.

d. Fractionations and sampling of gases.

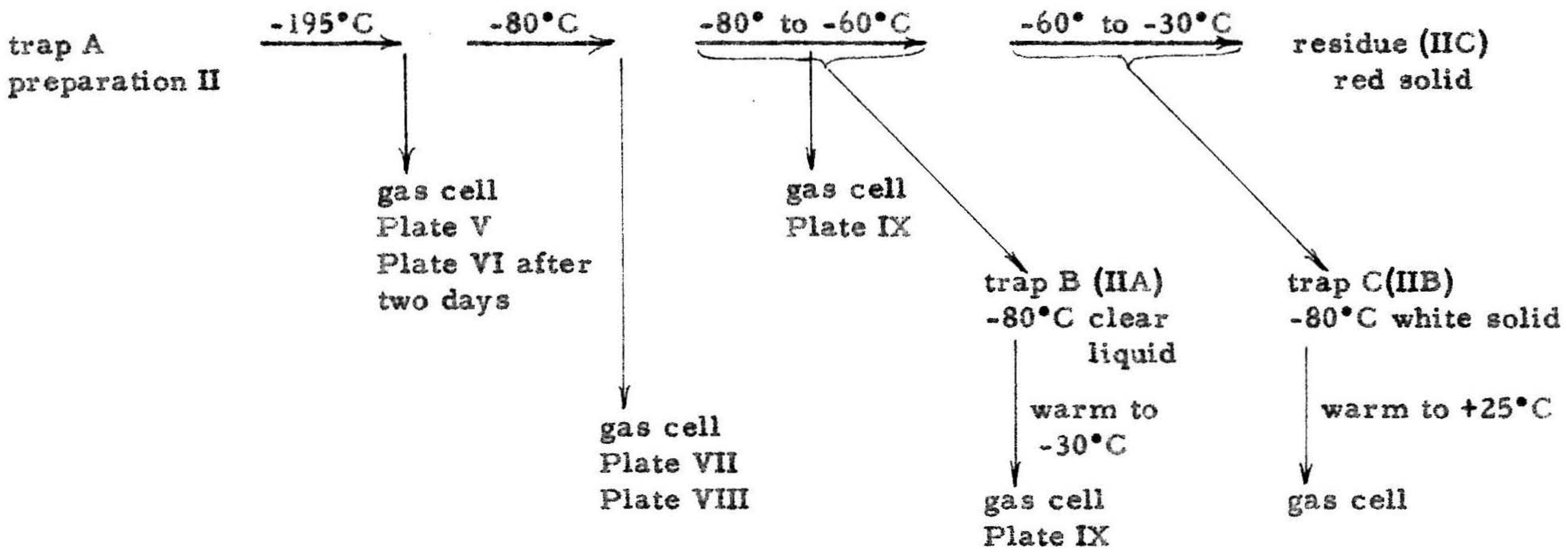
Flow Chart 1 shows the treatment of the first trial of the synthesis of the nitrogen-sulfur-fluorine compounds which were preparation I and preparation I (second heating). The method of taking a sample was to evacuate the gas cell and the manifold of the vacuum system shown in Figure II-4. The gas from the trap was allowed to expand into the gas cell. The stopcock of the gas cell was closed and it was removed from the system and the spectrum of the gas was taken. In Flow Chart 1 the temperature to which the material in trap A was allowed to rise is shown next to the arrow leading to the gas cell. The number of the plate which shows the spectrum of the sample is next to the words, gas cell.

In Flow Chart 2 the treatment of preparation II is shown. The



For further treatment of
preparations II and III
see Flow Charts 2, 3, and 4

Flow Chart 1


trap A
preparation II
-195°C
-80°C
-80° to -60°C
-60° to -30°C
residue (IIC)
red solid
gas cell
Plate V
Plate VI after
two days
gas cell
Plate IX
trap B (IIA)
-80°C clear
liquid
trap C(IIB)
-80°C white solid
gas cell
Plate VII
Plate VIII
warm to
-30°C
warm to +25°C
gas cell
Plate IX
gas cell

Flow Chart 2

temperature changes of trap A are recorded on the series of horizontal arrows. The sloping arrows indicate the removal of the fractions over the temperature range included by the brace. The designation of the receiving trap and its temperature are given at the end of the arrow. The designation of the fraction is in parentheses next to the trap designation. The physical nature of the collected fraction is also noted. A vertical arrow indicates the taking of a sample into the gas cell in the manner described above. The temperature at which the sample was taken is next to the vertical arrow. The plate number, if any, of the spectrum of the sample is just below the words, gas cell.

IV. Assignment of bands.

It was quickly found that the various preparations were contaminated by unwanted byproducts. It may have been fortunate that the first preparation produced a large amount of an easily identifiable impurity, SO_2, since it caused the investigator to be alert to the possibility of other impurities in later syntheses.

The first step in determining the nature of the impurities was to consider all possible compounds that could be formed from the interactions of C, N, O, F, Si, S, and Cl since the system contains N_4S_4, CCl_4, O_2, AgF_2, and SiO_2. The predominant ones would be those of C, N, F, and S. The infrared spectrum of each of the assumed compounds was sought in the literature and Table IV is a resume of that search. The three to five most intense bands are listed in order of decreasing intensity. If any band structure has been observed the character of the structure is indicated just below the frequency.

The steps in the identification of impurities were:

1. The bands of a spectrum were examined to see if any corresponded

with an impurity band in frequency and in band structure if this was resolvable.

2. If such a band was found then the spectrum was searched for other bands of the same impurity.
3. If other bands were found to correspond in frequency with those of the impurity they were checked to see if they corresponded in relative intensity.
4. If the relative intensities and band structures of the observed bands agreed with those of the impurity it was presumed to be identified.

Plate I shows the spectrum of the product from preparation I, first heating. The two strongest bands at 795 and 775 cm^{-1} were found to be those of CCl_4. The 795 cm^{-1} band is so intense that the absorption is essentially 100% and its intensity relative to the 775 cm^{-1} band is therefore not known exactly. The 775 cm^{-1} band has the proper envelope for the corresponding band of CCl_4. It is not surprising that CCl_4 should escape from the reaction system into the cold trap as its vapor pressure is 100mm at 23°C (76), the temperature of the condenser water. The 1360 cm^{-1} and the 850 cm^{-1} bands were not identified at this time because of their low intensity.

Plate II shows the spectrum of the product of the second heating of preparation I. Excluding the broad absorption between 12μ and 13.5μ the strongest band is at 1360 cm^{-1}. In this spectrum it is so intense that it is just barely possible to distinguish the PQR structure above the background noise. This band was tentatively attributed to SO_2 because of the large PR separation of 28 cm^{-1} and the frequency. The other stretching frequency of SO_2 lies at 1150 cm^{-1} and is the less intense. The corresponding band exhibits only P and R branches with a separation of 28 cm^{-1}.

It can easily be seen that such a band does exist at 1150 cm^{-1} fitting all the specifications. Thus SO_2 is identified as a major impurity.

It was this identification that prompted the construction of Table IV.

The next most intense band lies at 850 cm^{-1}. The actual intensity is uncertain as it lies on the shoulder of a broad absorption between 750 and 830 cm^{-1}. On the basis of its frequency it was tentatively assigned to $CFCl_3$. The next most intense band of $CFCl_3$ is a doublet at 1072 and 1085 cm^{-1}. In Plate II no doublet structure was resolved but a peak appeared at 1085 cm^{-1} with a wider shoulder extending towards lower frequency. This served tentatively to identify $CFCl_3$ as a component of the mixture. In Plate VIII the doublet is resolved and the identification is confirmed.

At this time the strong bands at 640 and 1530 cm^{-1} were unidentified as were the weaker bands at 905, 930, 1255, and 1625 cm^{-1} and as were the very weak bands at 730, 865, 885, and 890 cm^{-1}. Later observations showed that of these the 930 cm^{-1} band and all the very weak bands were attributable to impurities. The remainder will be discussed at length later.

The spectrum of the same sample was run a day later and is shown in Plate III. Several changes were observed. The band at 640 cm^{-1} had decreased slightly in intensity. A decrease in the 905 and 1255 cm^{-1} bands was less obvious but was detectable. The most striking change was the appearance of an intense band at 1030 cm^{-1}. Initially this was thought to be a band of SNF as was reported by Gallup and Koenig (49). On consulting the table of possible impurities it was found that the frequency matched precisely the frequency of the main band of SiF_4. The asymmetric shape of the band corresponded to that given in the literature (75).

The appearance of SiF_4 in view of its initial absence can be explained by the reaction of some fluorine containing material with the

Table IV

Bands of Possible Impurities in SNF and NSF_3 Synthesis.

Compound	Frequencies (cm^{-1})	Band structures and PR separations (cm^{-1})		Ref.
CCl_4	795	772 PQR 8		57
$CFCl_3$	845	1085 1072	930 PQR 15	58
CF_2Cl_2	1095 PQQR 14	1155 PQR 19	920 PQR 15	58
CF_3Cl	1210	1102 PQR 20	783 PQR 21	58
CF_4	1283 PQR 10	2187	632 PQR 38	59
COF_2	1249 PQR 20 1941 PQR 20	968 PQR 20 775 45	676 584	60
COS	859	2079		61
N_2F_2 trans	995			
" cis	952 PQQR 27	896 PR 18	737 PQR 28	62
N_2F_4	1025-930	735		36
NF_3	907 PQR 10	1031 PQR 45	642 PQR 40	63
NOF	766 PQR 32	1844 PQR 32	521	64
OF_2	831 PQR 27	928 PR 30		65
SF_4	728 PQR 23	867 PQR	889 PQR 20	66
SF_6	940	984	875	67
S_2F_{10}	940	827	890	68

Table IV (continued)

Compound	Frequencies (cm^{-1})	Band structures and PR separations (cm^{-1})		Ref.
SOF_2	748 PQQR 25	1333		69
	808 PQR 25			
SOF_4	821	928	1383	44
SOF_6	935	888		44
SO_2F_2	1502 PQR 25	848 PQR 21		70, 71
	885 PQR 24	1269 PQR 25		
SO_2	1360 PQR 28	1151 PR 28	518 PR 28	72
ClF	772 PR 28			73
ClF_3	703 PR 19	741 759		74
SiF_4	1031 PQR 11	1161	1294	75
		1191		

Plate III. Spectrum of same sample as shown in Plate II, taken 24 hours after Plate II

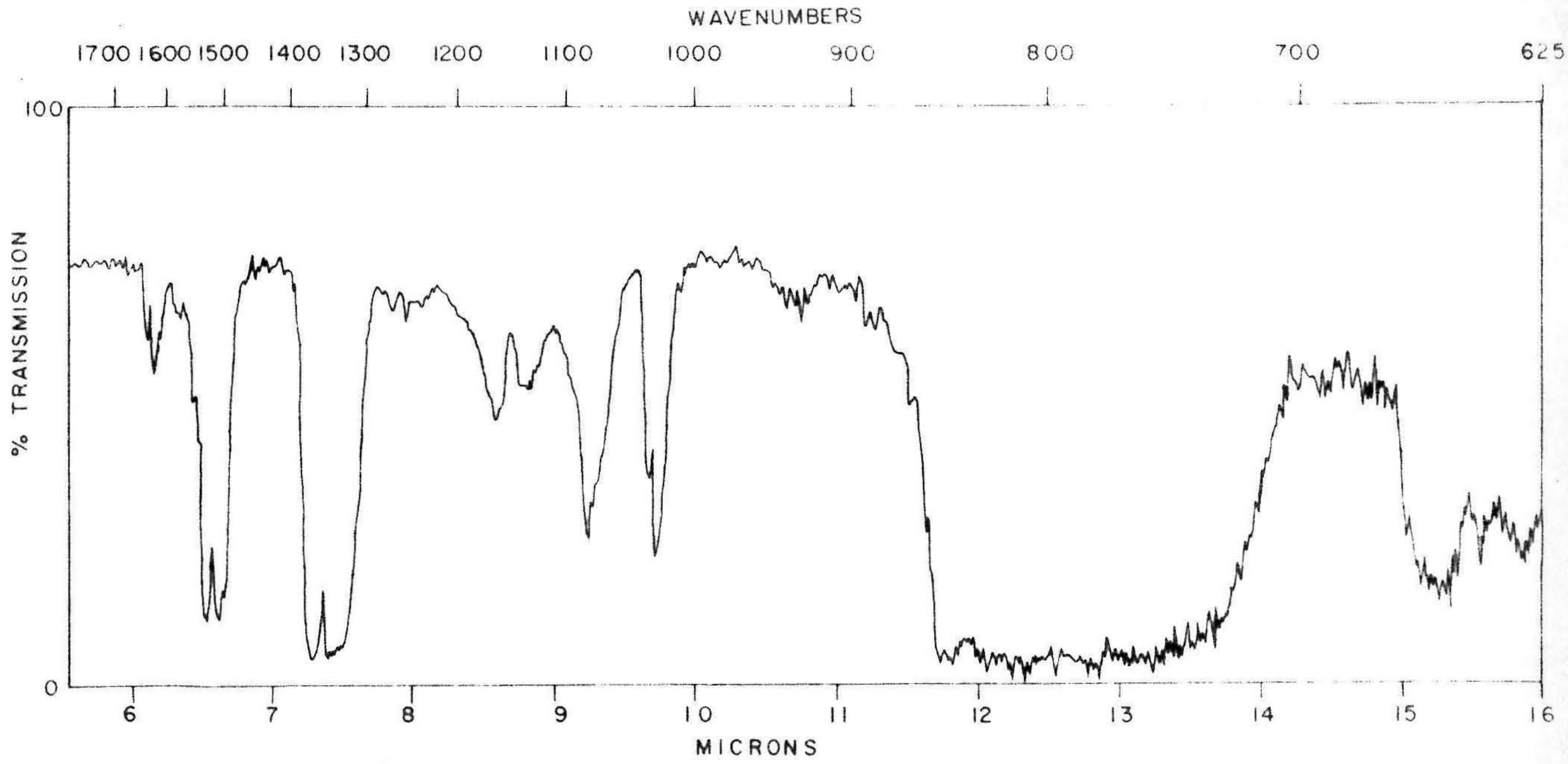

WAVENUMBERS
1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 625
100
% TRANSMISSION
0
6 7 8 9 10 11 12 13 14 15 16
MICRONS

Plate III.

glass of the gas cell. Ketelaar, Buchler, and Heslop in a recent note pointed out that glass cells containing inorganic fluorides often were attacked to form SiF_4 and eventually this reacts with the window material (NaCl or KBr) to form $SiF_6^{=}$ (77). It was also observed that a broad window peak appeared at 735 cm^{-1} in a cell that had KBr windows. The appearance of SiF_4 is accompanied by the decrease of three unknown bands and thus it would seem that the above explanation is appropriate. The three bands are therefore likely candidates for assignment to nitrogen-sulfur-compounds.

After the above sample had been in the gas cell for two days a yellow-green deposit appeared on the inner walls and windows of the cell. This corresponds to the observation of Glemser regarding his mixtures of SNF and SN_2F_2 (26). The yellow-green compound that he obtained he later investigated and found to be $S_3N_2F_2$ (27).

The cell was evacuated to see if there were any window bands which might be attributed to $S_3N_2F_2$. There were none. The cell was refilled with gas by allowing the reservoir trap to warm up to approximately -40°C and letting the gas expand into the cell. In Plate IV the total pressure of the gas can be seen to be much lower than in the sample shown in Plate II. It is curious that no bands appear at 640 or 1530 cm^{-1}. The bands at 850 and 730 cm^{-1} are now resolvable. The band at 795 cm^{-1} is obviously CCl_4 and it was to be expected. Two weak bands are now observable at 775 and 820 cm^{-1}.

Preparation II was synthesized and treated according to Flow Chart 2. The trap containing preparation II was held at -195°C by a liquid nitrogen bath and the gas from preparation II was allowed to expand into the evacuated gas cell. The spectrum of this sample is shown in Plate V.

Plate IV. Spectrum of gas given off at -40°C from preparation I (second heating)

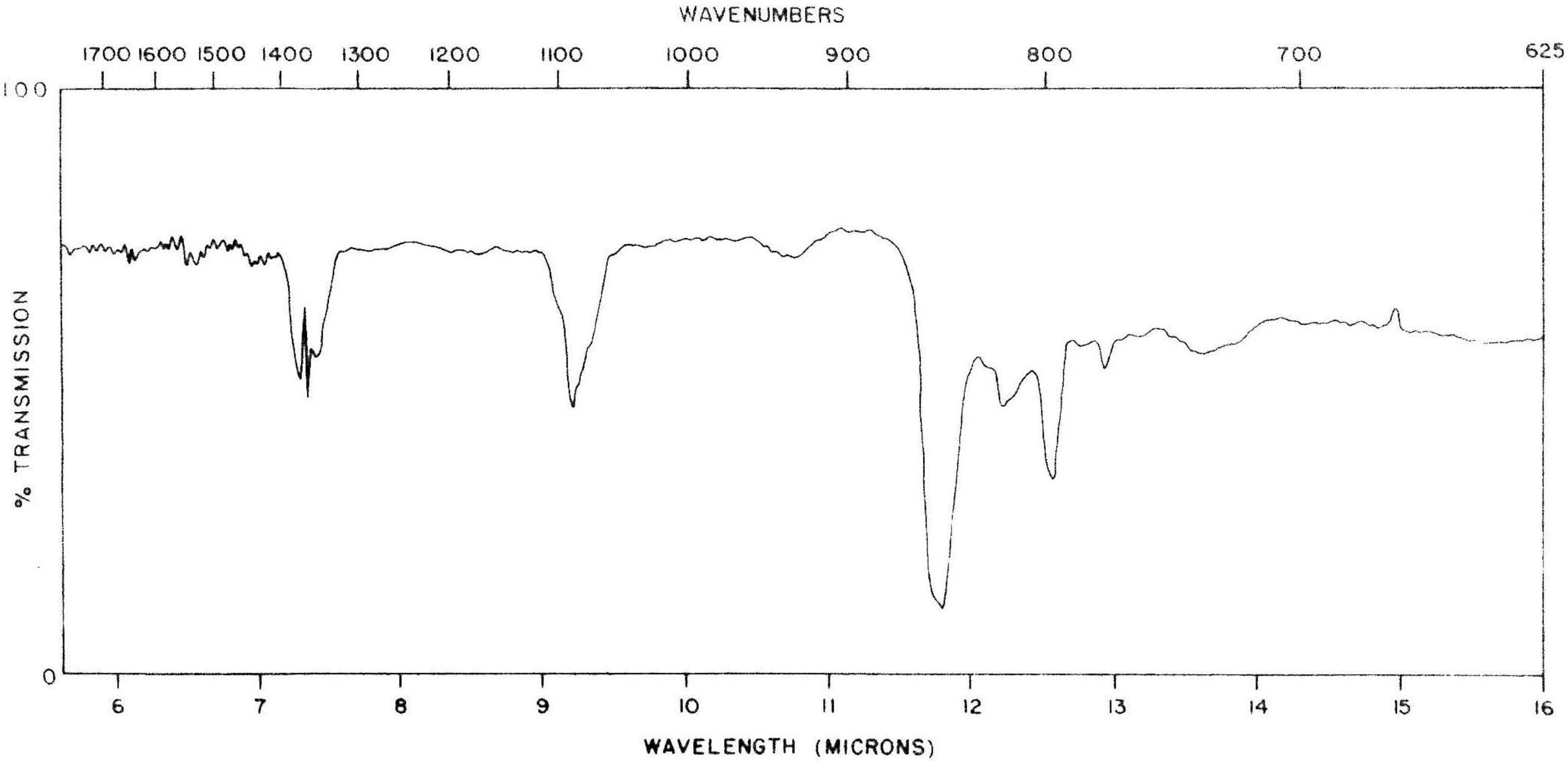
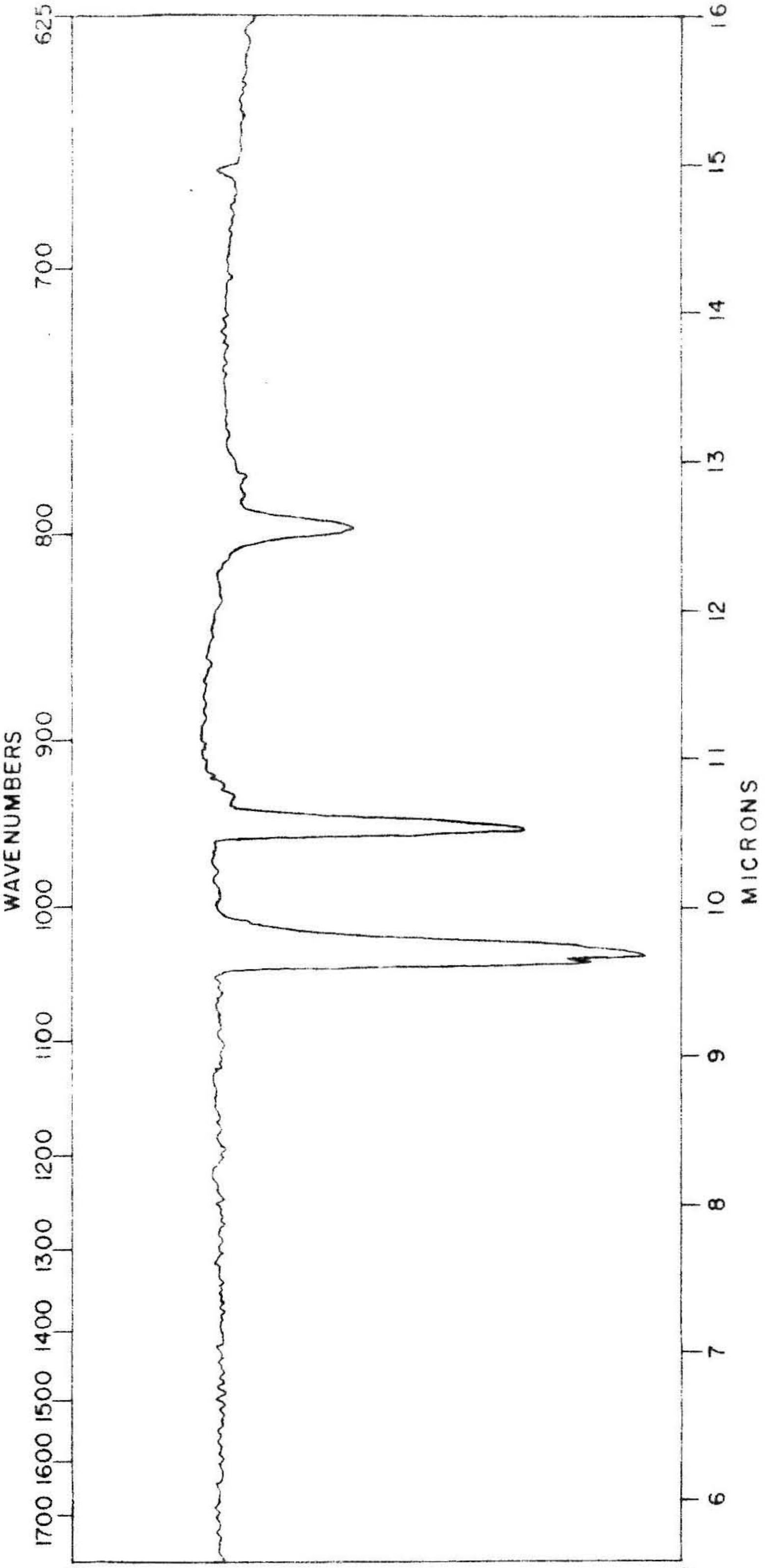

WAVENUMBERS
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
625
100
% TRANSMISSION
0
6
7
8
9
10
11
12
13
14
15
16
WAVELENGTH (MICRONS)

Plate V. Spectrum of gas given off at -195°C by preparation II


WAVENUMBERS
625
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
MICRONS
16
15
14
13
12
11
10
9
8
7
6
% TRANSMISSION
100
0

There are three bands at 795, 940, and 1030 cm^{-1}. Since the identification of impurities other than SO_2 and CCl_4 had not started at this point the compounds giving rise to the 940 and 1030 cm^{-1} bands were not known. Since these were the two bands assigned by Gallup and Koenig to SNF, it was decided to follow the time dependence of their intensities. If these were the bands of SNF they should both decrease with time as it decomposed. After two days the spectrum shown in Plate VI was taken. It is evident that the 1030 cm^{-1} band had decreased while the 795 and 940 cm^{-1} bands had remained constant. Also a large broad band centered at 735 cm^{-1} appeared. This band was found to remain after the cell was evacuated and must be due to some material on the windows. It was observed that the windows had become cloudy. The different behavior of the 940 and 1030 cm^{-1} bands made the conclusion inescapable that they belonged to two different compounds.

As was later found the 1030 cm^{-1} was the main band of SiF_4 and the window peak at 735 cm^{-1} was caused by the product of the reaction of SiF_4 with the KBr windows. In cells with NaCl windows the window peak appeared at 720 cm^{-1}. It cannot be determined if the difference in the frequencies is a result of the $SiF_6^{=}$ being in different crystal lattices or if $SiF_4Cl_2^{=}$ and $SiF_4Br_2^{=}$ are the species formed.

In Table IV the two possible compounds having their most intense bands at 940 cm^{-1} are SF_6 and S_2F_{10}. S_2F_{10} is produced in small quantities during the fluorination of sulfur. The sulfur -sulfur bond in S_2F_{10} comes from fluorination of S_2 fragments of the S_8 ring in sulfur (78). On the basis that S_2F_{10} is unlikely to appear in large quantities and that the probability of producing S_2F_{10} is small, N_4S_4 having no sulfur -sulfur bonds (79), the 940 cm^{-1} band was assigned to SF_6.

Plate VII shows the spectrum of the gas given off when the reservoir

Plate VI. Same sample as Plate V, two days later.

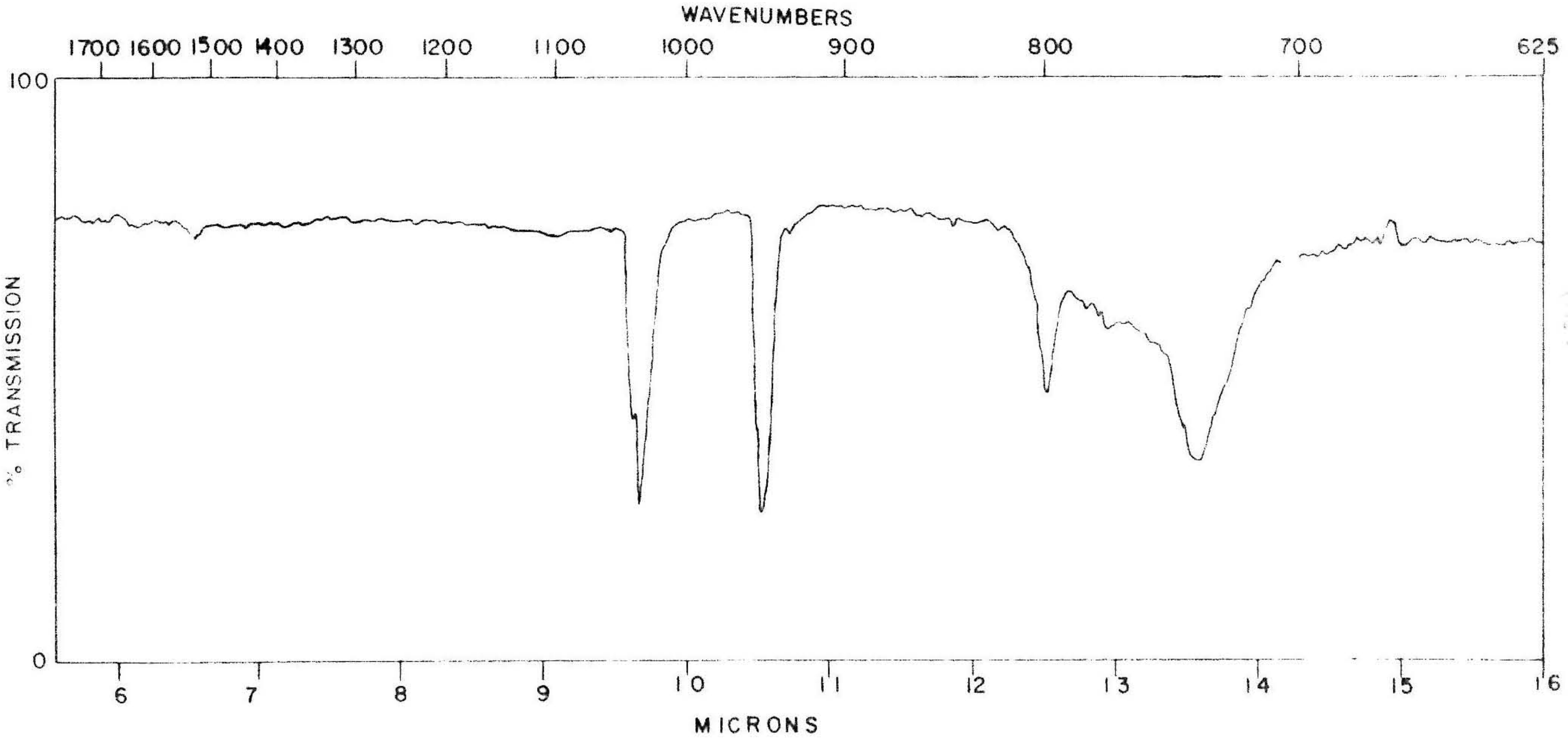

WAVENUMBERS
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
625
100
0
% TRANSMISSION
6
7
8
9
10
11
12
13
14
15
16
MICRONS

Plate VI.

Plate VII. Spectrum of gas given off at -80°C by preparation II

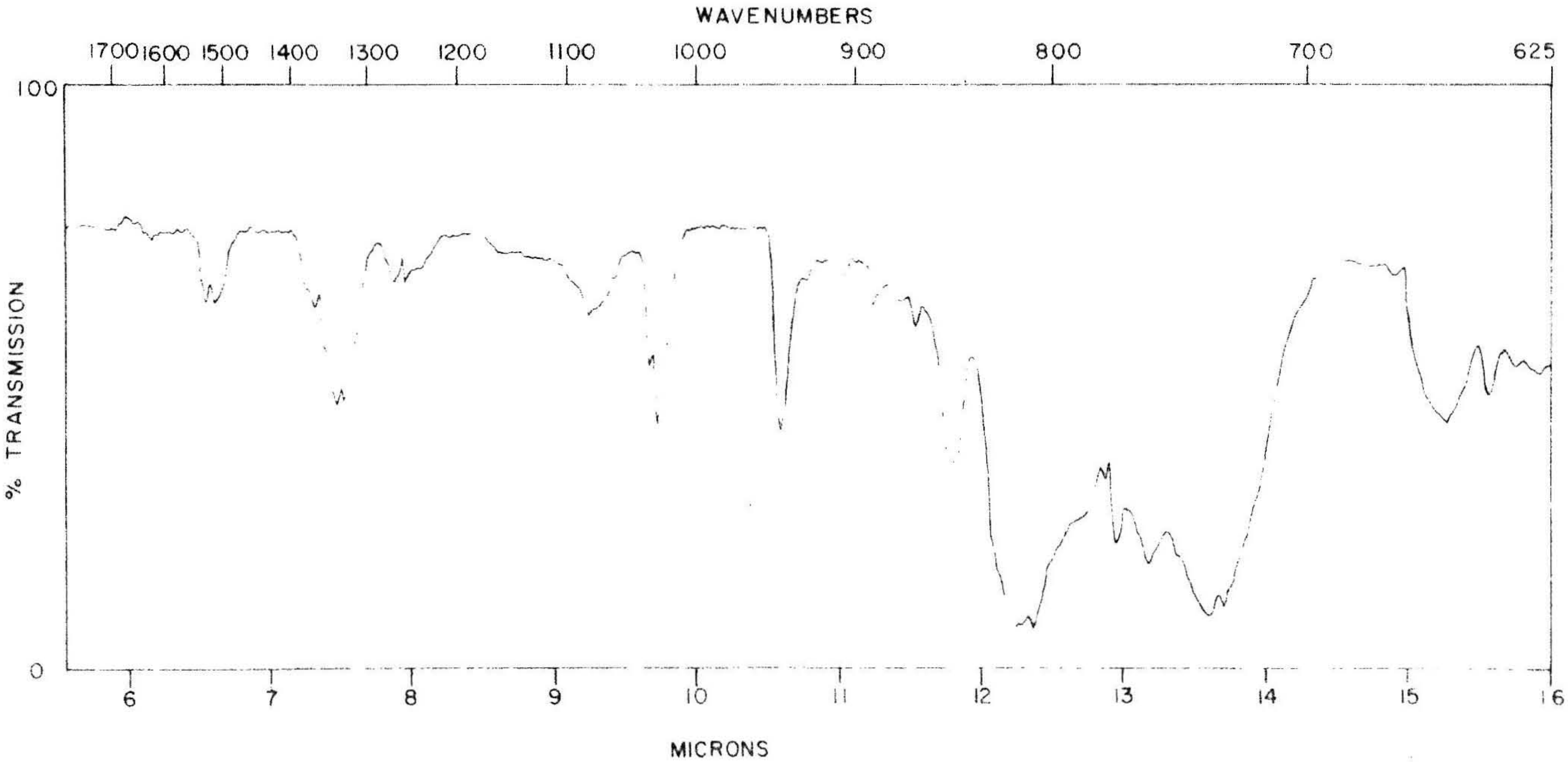

WAVENUMBERS
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
625
100
0
% TRANSMISSION
6
7
8
9
10
11
12
13
14
15
16
MICRONS

Plate VII.

trap containing preparation II was held at -80°C. Present and previously identified were $CFCl_3$, SF_6, SiF_4, and the window peak which remained from the previous sample. Intense bands which had been previously observed were found at 640, 775, 820, and 1530 cm^{-1}. Somewhat weaker but also previously observed bands were at 730, 865, 890, 905, and 1255 cm^{-1}. A small peak was observed on the shoulder of the 820 cm^{-1} band at 808 cm^{-1}. Two bands that had heretofore been unobserved were those at 760 and 1160 cm^{-1}. The moderately intense band between 1300 and 1400 cm^{-1} was thought to be due to SO_2 but on examination with the Beckman IR7 it was found to consist of three bands at 1330, 1340, and 1370 cm^{-1}. The last is actually the R branch of SO_2, with the rest of the band overlapping the other two bands.

The search for possible impurities with intense bands at 730, 760, 808, 865, 890, 1160, and 1255 cm^{-1} (see Table IV) resulted in the assignment of a few of these bands to known compounds. The 730 cm^{-1} band could possibly belong to SF_4. Its next most intense bands are at 867 and 889 cm^{-1} (66)which correspond nicely with the 865 and 890 cm^{-1} bands observed here. These bands were therefore assigned to SF_4.

The 808 cm^{-1} band corresponds to one of the two intense bands of SOF_2. The other band at 748 cm^{-1} should be equally intense but in Plate VII only a weak bump appears on the shoulder of the large window peak at 735 cm^{-1}. This is not conclusive evidence against this assignment as the true intensity is obscured by the presence of the window peak. The 1330 cm^{-1} band is present and is presumably the 1333 cm^{-1} band reported by O'Loane and Wilson (69).

At this point unidentified bands had been observed at 640, 760, 775, 820, 905, 1160, 1340, 1525, and 1630 cm^{-1}. No assignments of these bands to different compounds could be made until some purification of the various components could be carried out.

Plate VIII was run on the IR7 and is the spectrum of the same sample examined in Plate VII. The grating instrument permitted a more precise measurement of the frequencies. The centers of the unassigned bands were found to lie at 644, 758, 774, 819, 907, 1257, 1340, 1520, and 1625 cm^{-1}. The bands at 644 cm^{-1} and the ones at 907 and 1257 cm^{-1} were found to have P, Q, and R branches with PR separations of 26 and 26 cm^{-1} respectively.

Twenty-four hours later, after running the spectra in Plates VII and VIII it was observed that the 644 cm^{-1} band had disappeared and the bands of SiF_4 and SF_4 had decreased somewhat. Three hours later the SiF_4 and SF_4 bands had disappeared completely. In addition the 758, 907, and 1257 cm^{-1} bands had disappeared. The SO_2 bands had increased by a moderate amount.

At this point the residuum of preparation II was separated into fractions IIA, IIB, and IIC (see Flow Chart 2). The spectrum of fraction IIC showed only the bands of CCl_4 and SiF_4 while the spectrum of fraction IIB contained only the bands of $CFCl_3$, CCl_4, and a small amount of SO_2. The spectrum of fraction IIA strongly resembles the spectrum shown in Plate VII and is shown in Plate IX. There are several differences, however. First the bands of SiF_4 and SF_6 are absent. The intensities of the 907 and 1257 cm^{-1} bands are much stronger than in the earlier spectrum while the 1340 cm^{-1} is much weaker. A weak new band was observed at 1375 cm^{-1}. Plate X shows this band at higher resolution. Unfortunately it is obscured somewhat by the SO_2 band. This band was found to be present only when there was a large absorption of the 644 cm^{-1} band.

Preparation III was synthesized and treated as is shown in Flow Chart 3. The spectrum of fraction IIIA was run and found to be essentially the same as that shown in Plate VII.

Fraction IIIB' was found to consist of a relatively pure product. The

Plate VIII. (Three pages) - Spectrum of same sample examined in Plate VII.

Beckman 1R7 used

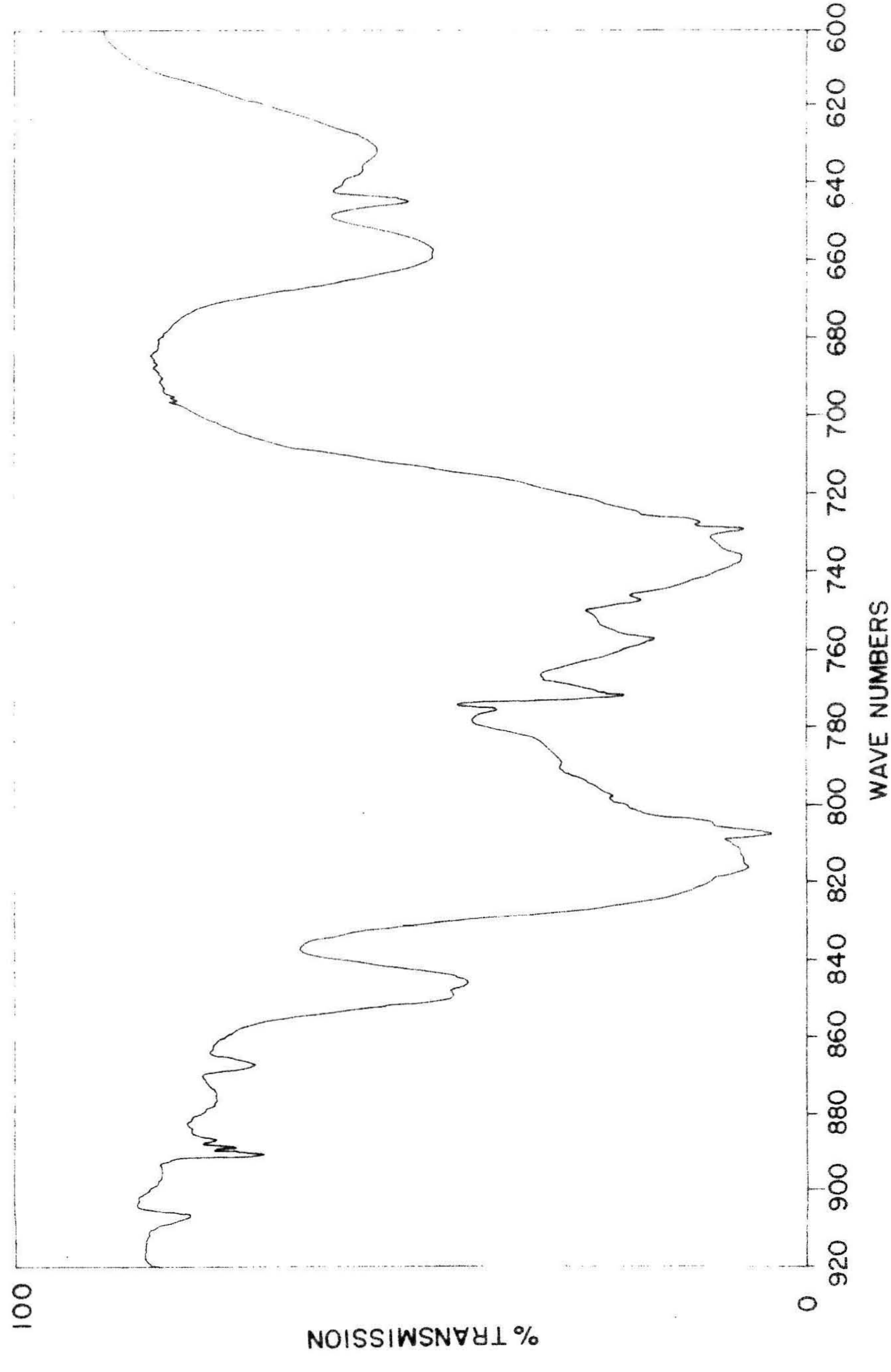

% TRANSMISSION
100
0
WAVE NUMBERS
920
900
880
860
840
820
800
780
760
740
720
700
680
660
640
620
600

Plate VIII.

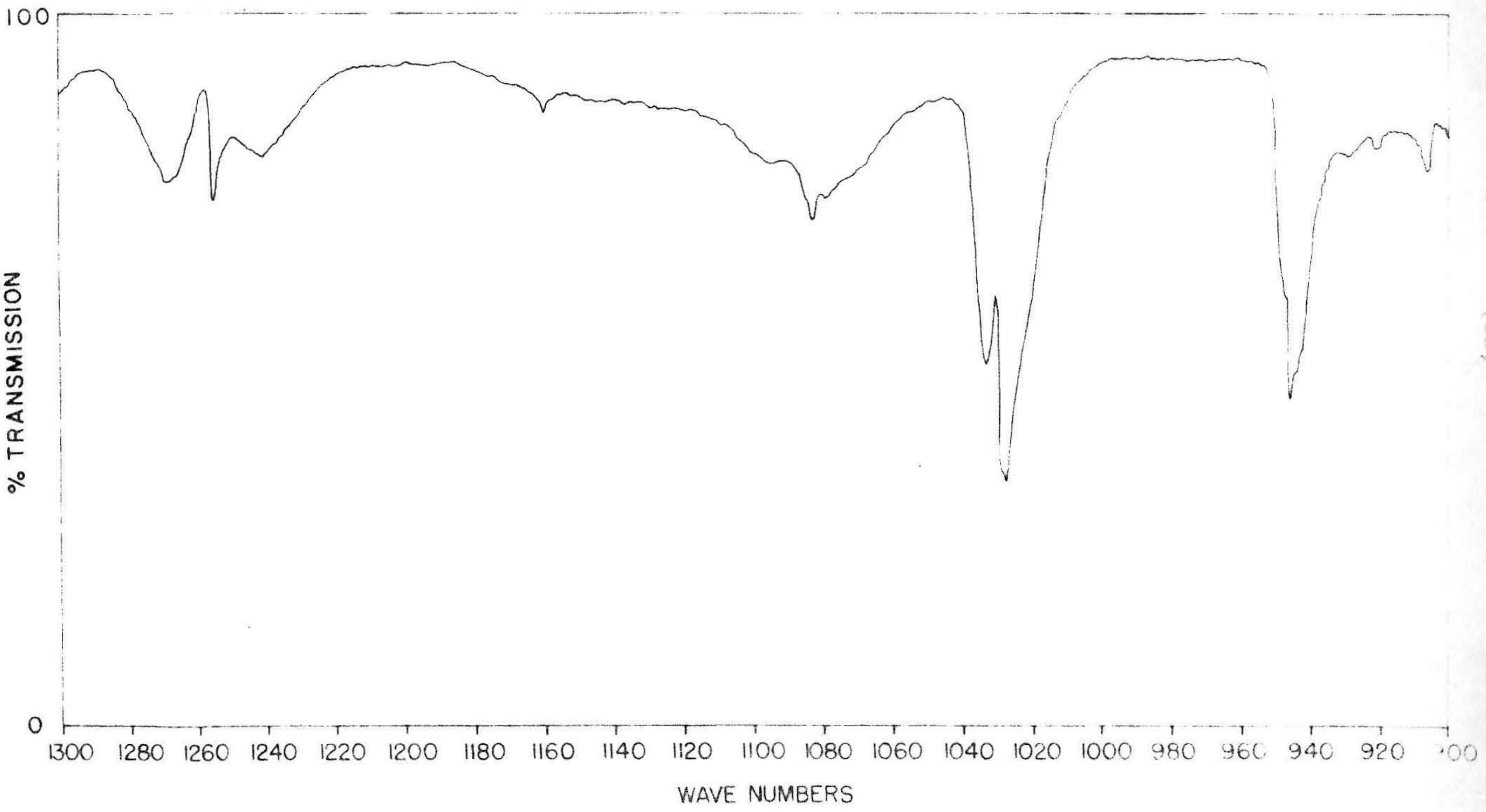

100
0
% TRANSMISSION
1300
1280
1260
1240
1220
1200
1180
1160
1140
1120
1100
1080
1060
1040
1020
1000
980
960
940
920
900
WAVE NUMBERS

Plate VIII.

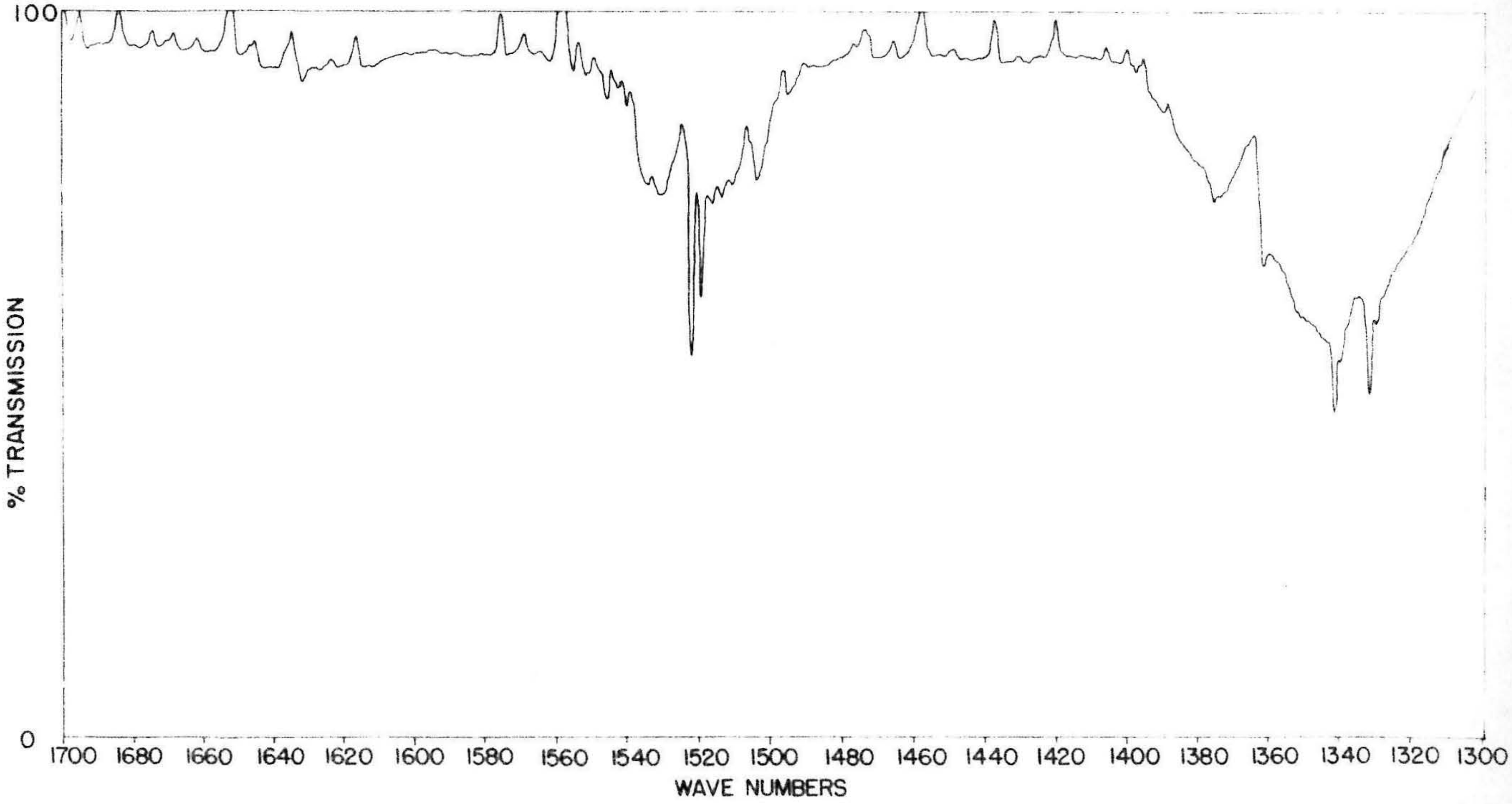

100
0
% TRANSMISSION
1700
1680
1660
1640
1620
1600
1580
1560
1540
1520
1500
1480
1460
1440
1420
1400
1380
1360
1340
1320
1300
WAVE NUMBERS

Plate VIII.

Plate IX. Spectrum of fraction IIA

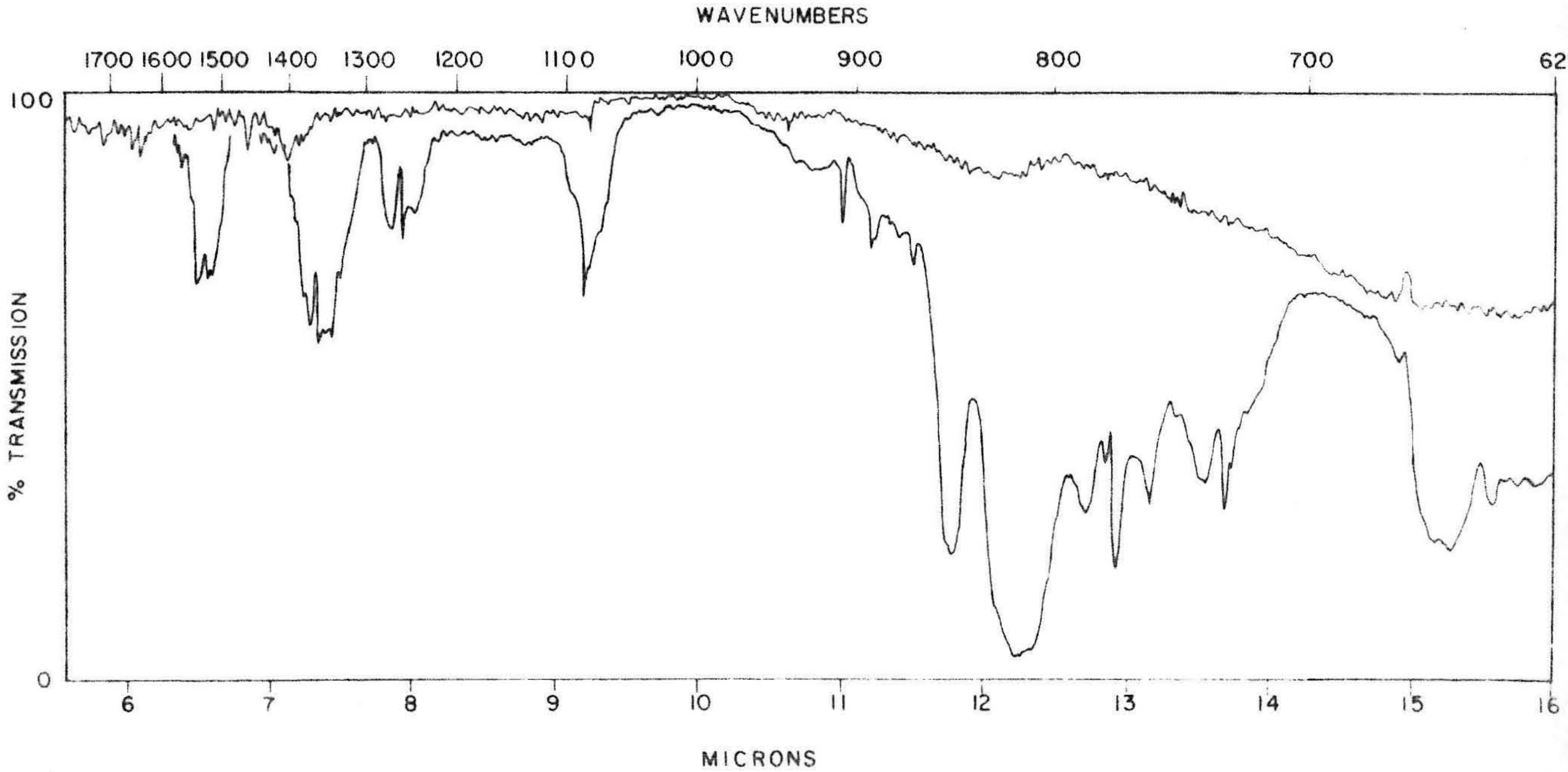

WAVENUMBERS
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
625
100
% TRANSMISSION
0
6
7
8
9
10
11
12
13
14
15
16
MICRONS

Plate IX.

Plate X. 1375 cm^{-1} band of SNF at high resolution

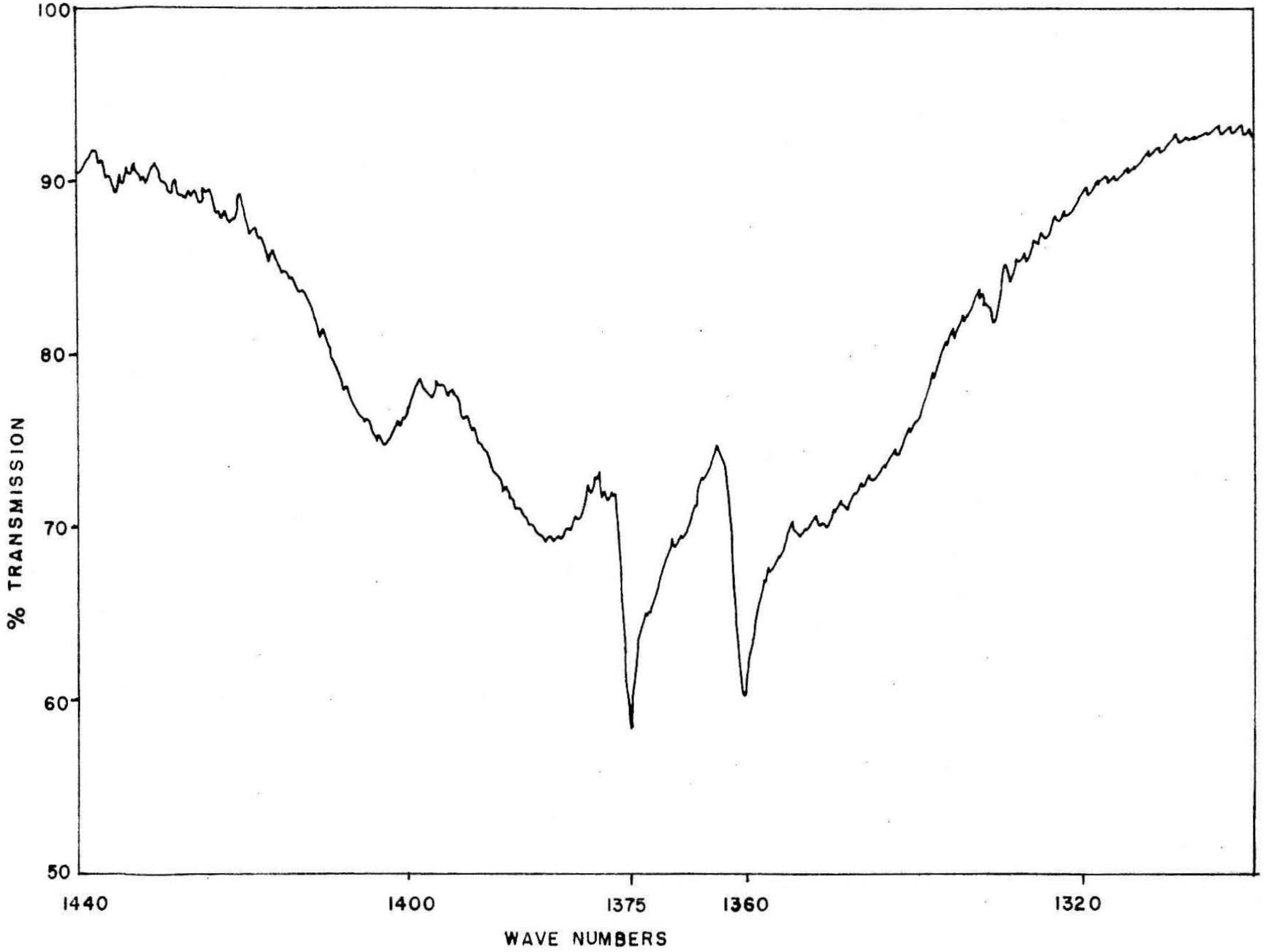
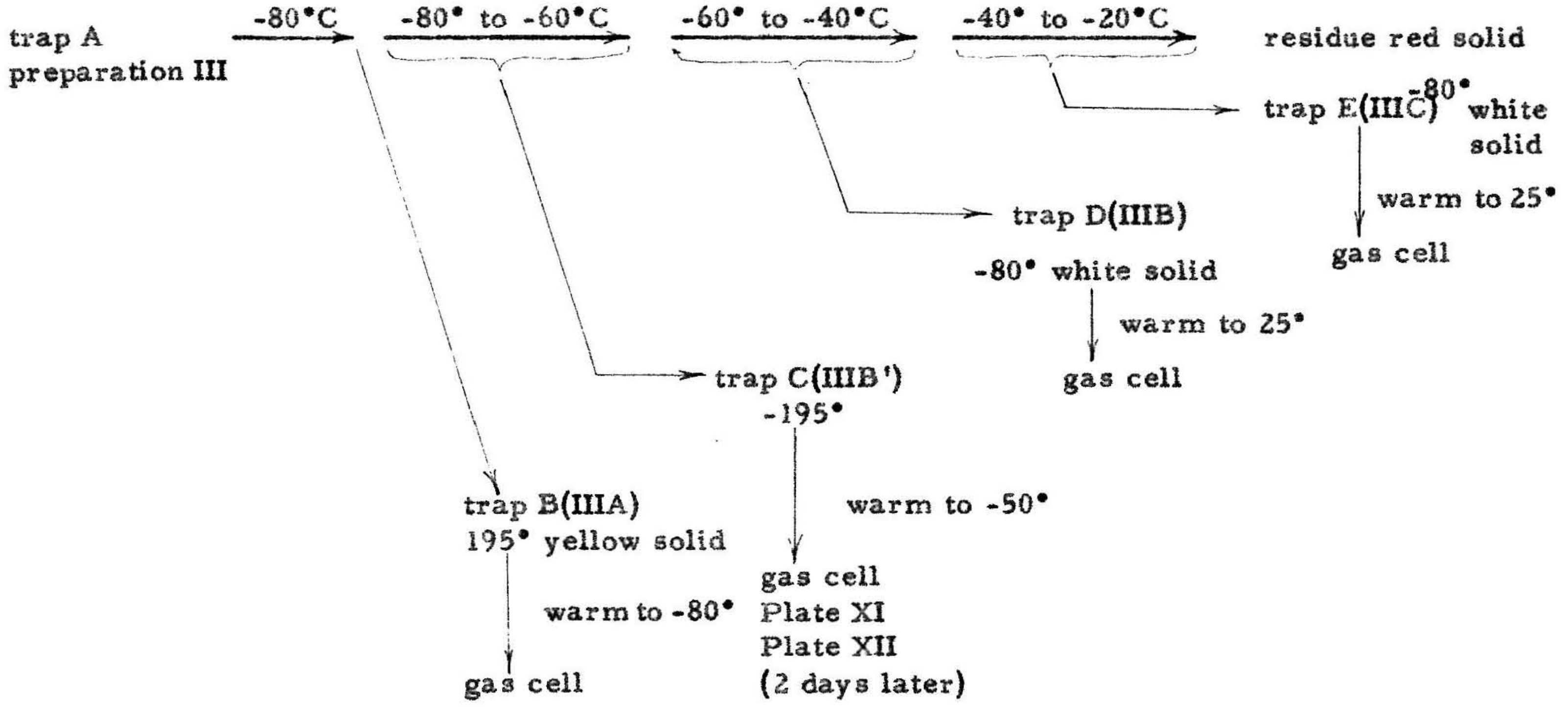

100
90
80
70
60
50
% TRANSMISSION
1440
1400
1375
1360
1320
WAVE NUMBERS

Plate X.


trap A
preparation III
-80°C
-80° to -60°C
-60° to -40°C
-40° to -20°C
residue red solid
trap E(IIIC) -80° white solid
warm to 25°
gas cell
trap D(IIIB)
-80° white solid
warm to 25°
gas cell
trap C(IIIB')
-195°
warm to -50°
gas cell
Plate XI
Plate XII
(2 days later)
trap B(IIIA)
195° yellow solid
warm to -80°
gas cell

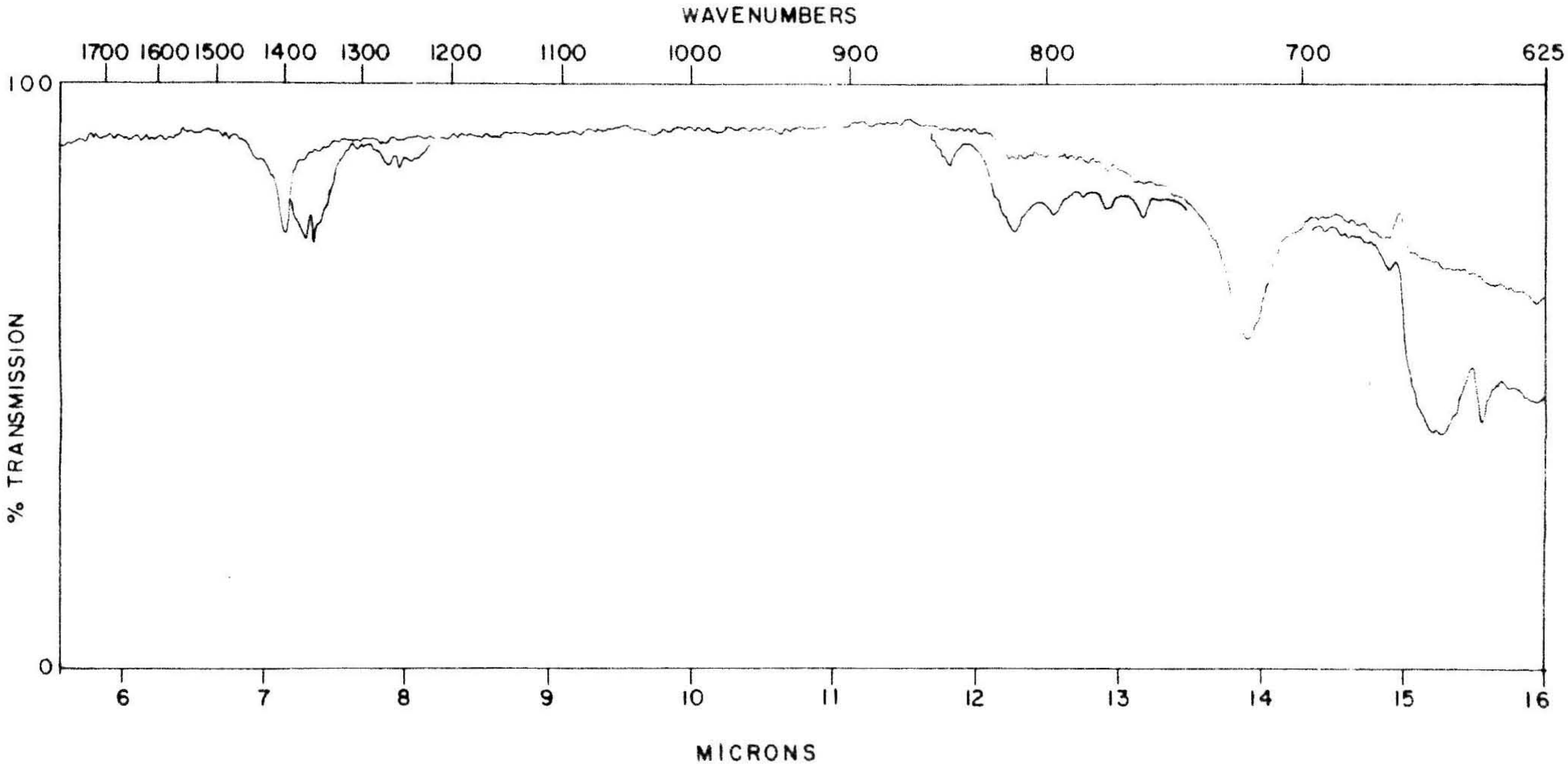
Flow Chart 3

spectrum of this fraction is shown in Plate XI. The upper curve is the background showing clearly a window band left over from the previous sample. Initially the major component of the mixture is the compound with the intense band at 644 cm^{-1}. This compound will be arbitrarily designated as compound A. Also present as weak absorptions are bands of SO_2 at 1360 cm^{-1}, CCl_4 at 795 cm^{-1}, $CFCl_3$ at 848 cm^{-1}, and SiF_4 at 1031 cm^{-1}. The weak bands at 774 and 819 cm^{-1} are assigned to the unknown compound designated as compound B. These bands of compound B are the most intense bands in the spectrum in Plate VIII.

As can be seen by comparing Plate XI with Plate XII, the spectrum of the same sample taken 48 hours later, the 644 cm^{-1} band of compound A diminishes in intensity and the bands of SO_2 and SiF_4 increase while three new bands appear at 758, 907, and 1257 cm^{-1}. As long as A is present the intensities of the SO_2, SiF_4, and the three new bands increase. The compound giving rise to the new bands was designated compound C. Looking back at Plates VII and VIII these same bands can be seen when A is present, but later when A has completely disappeared the bands of C have also vanished. The 907 and 1257 cm^{-1} bands were examined under high resolution; the P, Q, and R branches were readily discernable, but the rotational structure of these bands was not resolved. The PR separations of both bands were 26 cm^{-1}. There is no discernable P or R branch of the 758 cm^{-1} band since the window peak and the 774 cm^{-1} band of B overlap the regions where they would be expected to appear.

From these observations one can conclude that C is the daughter of A. When present by itself C is relatively stable and may persist for several days but in the presence of other materials it may disappear in less than 24 hours. It was found that the rate of increase of SO_2 concurrent with the formation of C was proportional to the increase in C. As C diminished

Plate XI. Spectrum of fraction IIIB'


WAVENUMBERS
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
625
100
0
% TRANSMISSION
6
7
8
9
10
11
12
13
14
15
16
MICRONS

[illegible]

Plate XII. Spectrum of same sample as Plate **XI**,
taken two days after Plate **XI**

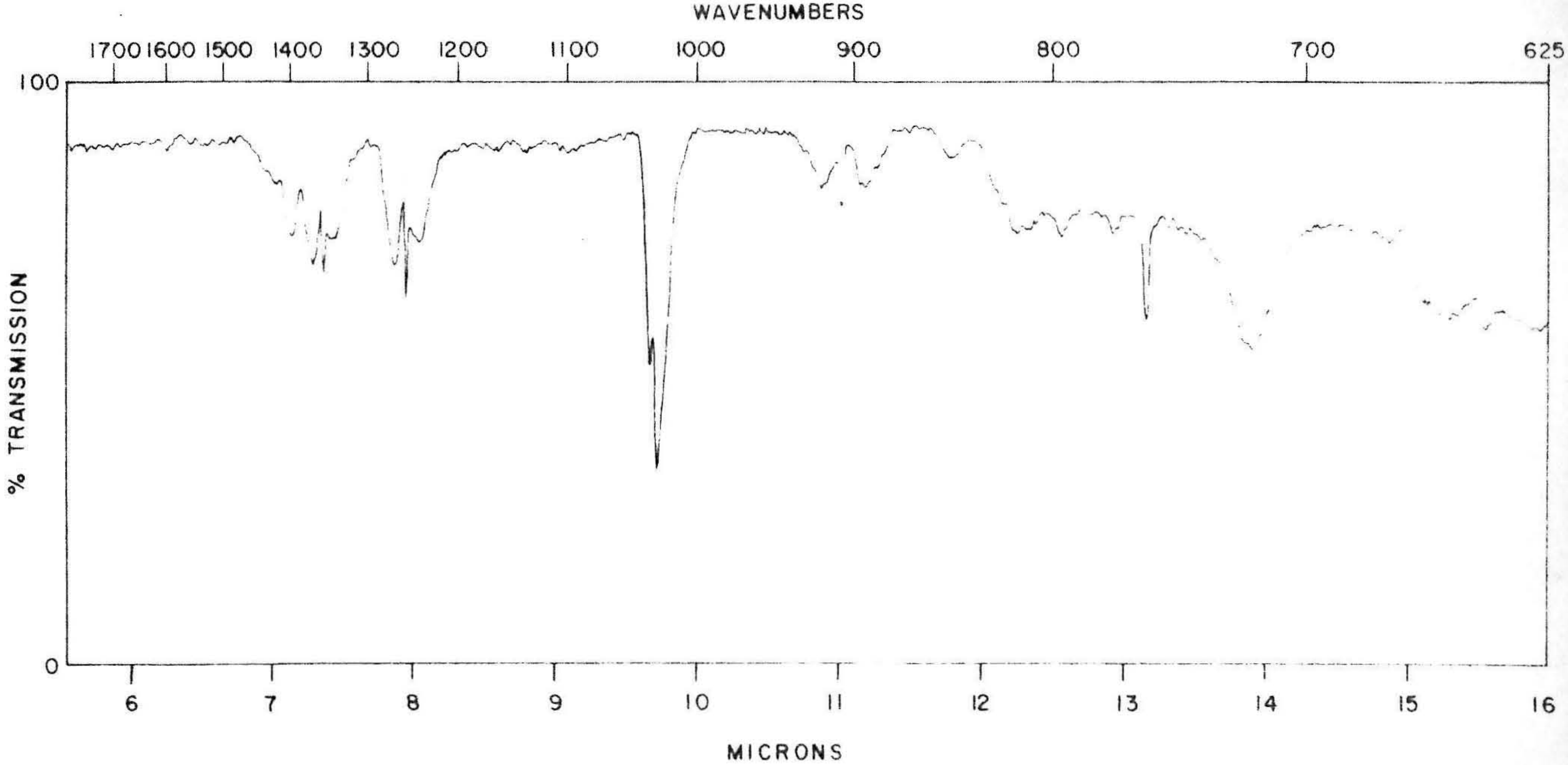

WAVENUMBERS
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
625
% TRANSMISSION
100
0
6
7
8
9
10
11
12
13
14
15
16
MICRONS

Plate XII.

the 1360 cm^{-1} band of SO_2 continued to increase until C had vanished completely.

Fraction IIIB showed predominantly the bands of A, B, $CFCl_3$, and SO_2. Fraction IIIC showed the bands of $CFCl_3$ and CCl_4 with a small intensity of the SO_2 band.

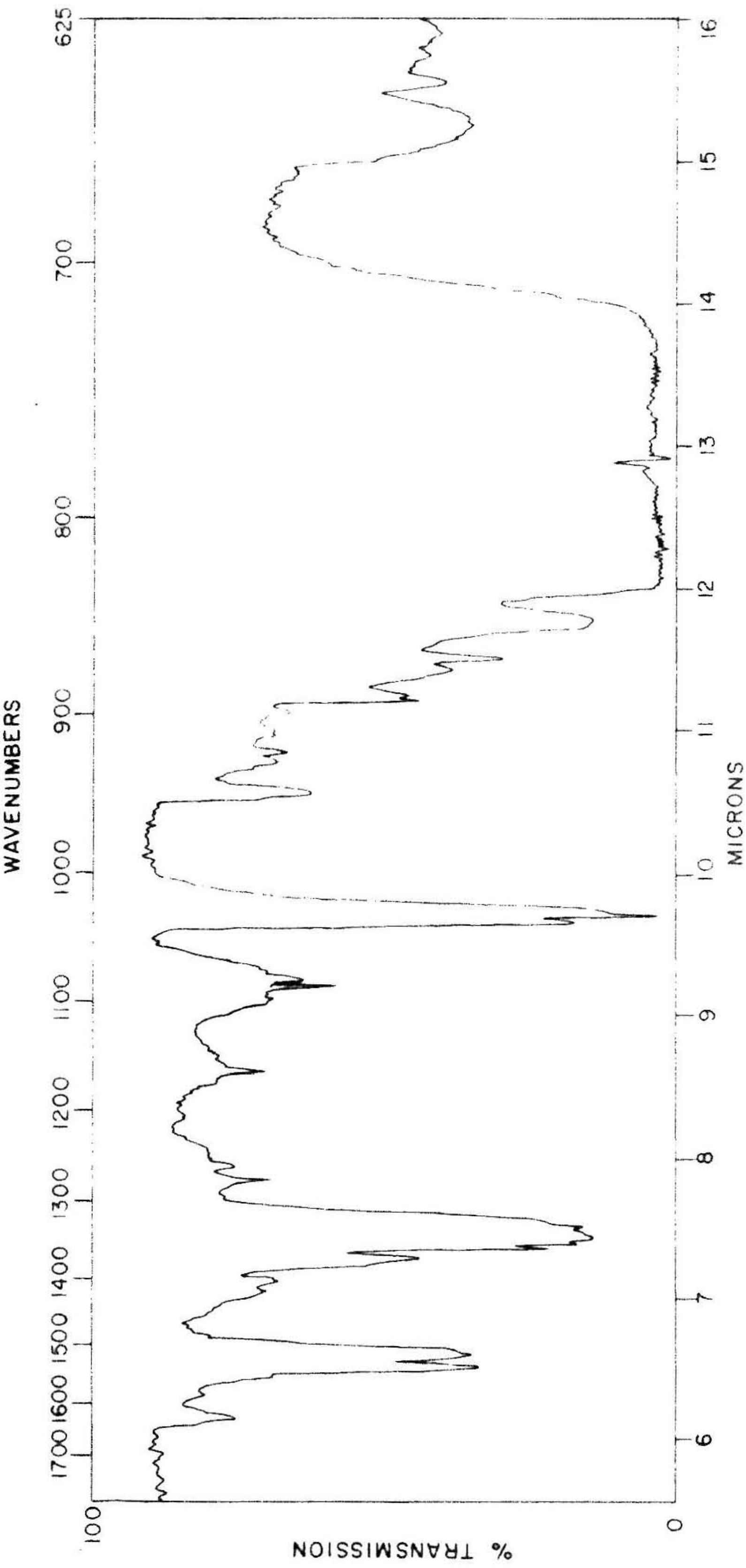
The spectra of the fractions showed that the compounds present could be split into three groups according to their relative volatility.

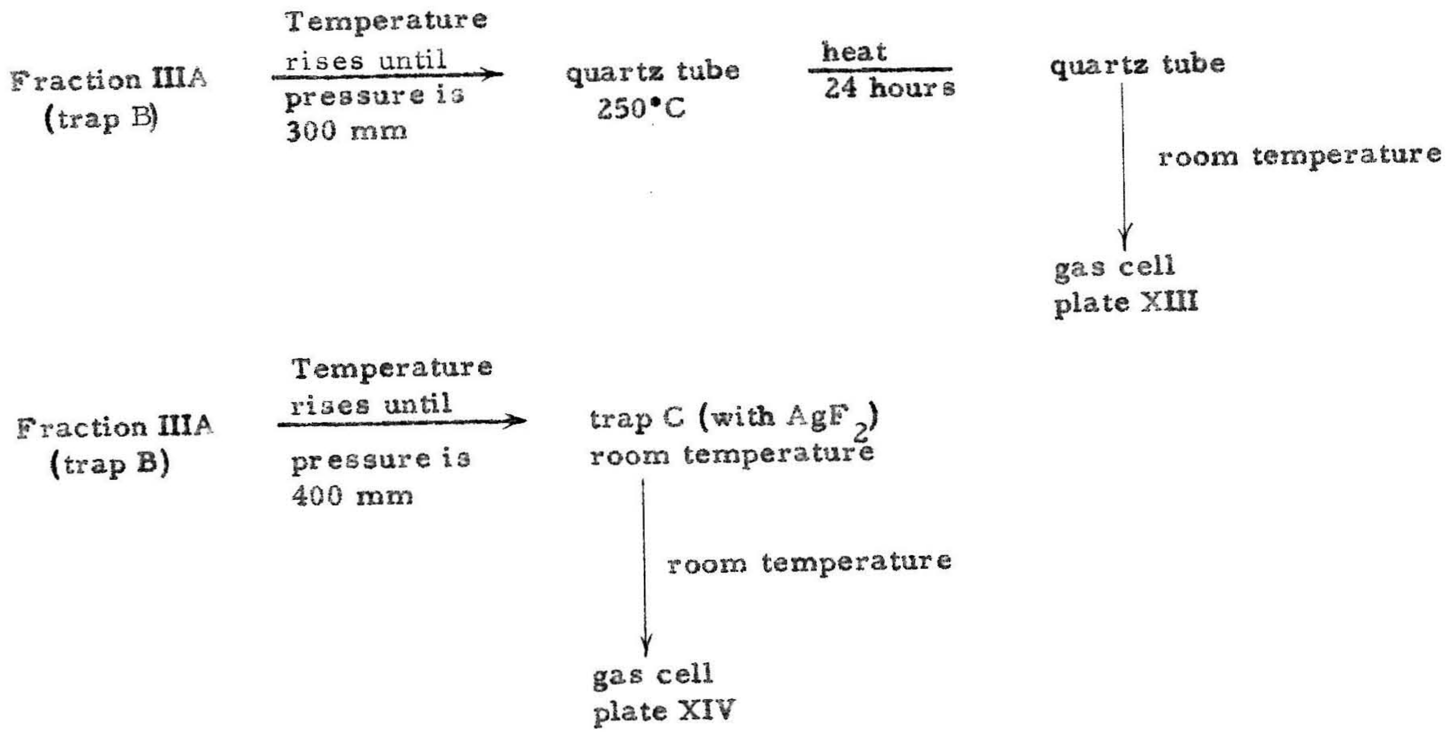
1. Most volatile: SiF_4, SF_6, SF_4, SOF_2.
2. Intermediately volatile: A, B, SO_2, ($CFCl_3$)
3. Least volatile: $CFCl_3$, CCl_4, (SO_2)

The $CFCl_3$ appears in two groups but is predominantly in group 3. SO_2 is approximately equally divided between groups 2 and 3. The highest boiling compound in group 1 is SF_4 b.p. -40°C and the lowest boiling member of group 3 is $CFCl_3$ b.p. 24°C. A and B very likely have boiling points in that range of temperatures.

Plate XIII shows the spectrum of a sample of fraction IIIA which had been pyrolyzed in a quartz tube for 24 hours (see Flow Chart 4). It can be seen that a considerable amount of compound A is present, but this may be a consequence of the large amount of A that was present in the starting material or it may be that some of compound A is being produced by decomposition of other compounds. However the presence of even a small amount of A is surprising as it is unstable even at room temperature and would be presumed to be less stable at elevated temperatures. Such large amounts of B are present that absorption is total between 700 and 850 cm^{-1}. $CFCl_3$ is present as shown by the presence of the 848 cm^{-1} band. SF_4 is also present (867 and 889 cm^{-1}) as is C (907 cm^{-1}). The other impurities are SF_6 (940 cm^{-1}) and SiF_4 (1031 cm^{-1}) which is present in large quantity. A sharp peak at 1160 cm^{-1} has been observed before but has not been

Plate XIII. Spectrum of pyrolyzed sample of fraction IIIA


WAVENUMBERS
625
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
MICRONS
16
15
14
13
12
11
10
9
8
7
6
% TRANSMISSION
100
0


Fraction IIIA
(trap B)
Temperature
rises until
pressure is
300 mm
quartz tube
250°C
heat
24 hours
quartz tube
room temperature
gas cell
plate XIII
Fraction IIIA
(trap B)
Temperature
rises until
pressure is
400 mm
trap C (with AgF$_2$)
room temperature
room temperature
gas cell
plate XIV

Flow Chart 4

assigned to any compound. This band is much more intense than has been observed in any other spectrum. The 1257 cm^{-1} band confirms the presence of C. The complex band between 1300 and 1400 cm^{-1} contains mainly the 1360 cm^{-1} of SO_2 with some of the 1333 cm^{-1} of SOF_2 and a large amount of the 1340 cm^{-1} band. It appears that the 1160 cm^{-1} and the 1340 cm^{-1} bands are correlated. The compound giving rise to these bands will be designated as compound D.

The peak at 1400 cm^{-1} was found to be a window peak. The 1520 and 1625 cm^{-1} bands have been observed before and they are tentatively assigned as the overtones of the 774 and 819 cm^{-1} bands of B. New bands that appeared at 920, 930, and 1270 cm^{-1} were unassigned.

A sample that had been pyrolyzed for four days showed no differences with the sample described above.

A sample of fraction IIIA was placed in a trap in contact with solid AgF_2 at room temperature at a pressure of 400mm for 24 hours. This is the method that Glemser used to convert SN_2F_2 to NSF_3. Plate XIV shows the spectrum of the product of this reaction. The bands of B at 774, 819, 1520, and 1625 cm^{-1} are present. The bands of $CFCl_3$, SiF_4, SF_6, and SO_2F_2 are also present. The large absorptions at 850, 890, 1270, and 1500 cm^{-1} are those of SO_2F_2. It appears that the effect of the AgF_2 was to fluorinate SO_2. Compound B was unaffected.

V. Discussion.

a. Assignments of bands to new compounds.

Eleven new infrared bands were found in the spectra of products of the fluorination of N_4S_4. These bands appeared not to belong to any compounds previously investigated. These could be divided into four groups within each of which the relative intensities appeared to remain constant

Plate XIV. Spectrum of product of reaction between fraction IIIA and AgF_2

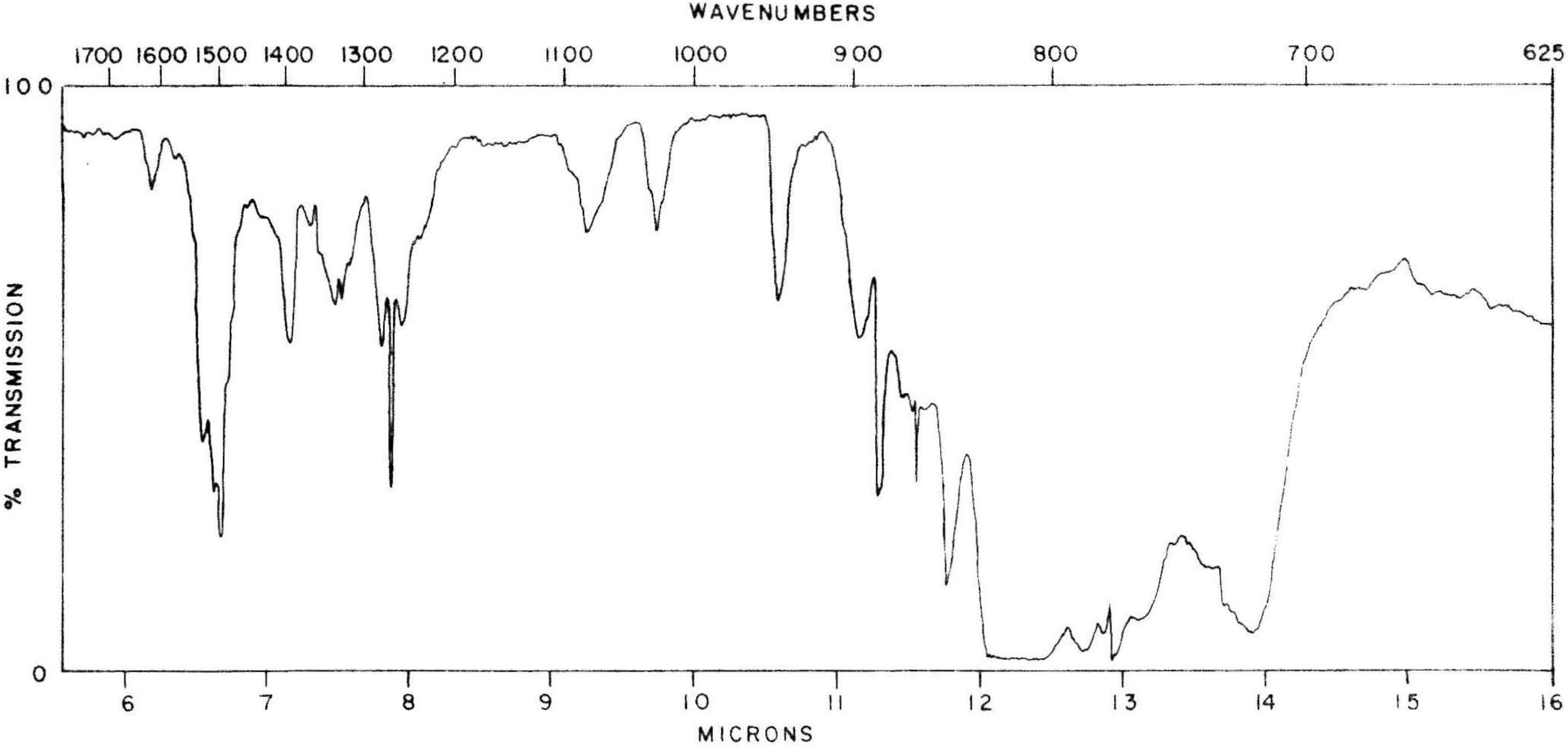

WAVENUMBERS
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
625
% TRANSMISSION
100
0
6
7
8
9
10
11
12
13
14
15
16
MICRONS

Plate XIV.

with varying conditions, though from group to group the intensities were variable. Consequently it seems reasonable to attribute these bands to four new compounds designated A, B, C, and D. Table V summarizes the assignments.

Table V

Assignment of Frequencies to Unknown Compounds

Compound	Frequencies cm^{-1}	Band structure and PR separation (cm^{-1})
A	644	PQR 26
	1375	Q (P and R branches overlapped by impurity bands)
B	774	PQR 26
	819	Q (broad)
	1520	PQR 20
	1625	PQR 20
C	758	(P)Q(R)
	907	PQR 26
	1257	PQR 26
D	1160	Q (P and R branches too weak to observe)
	1340	Q (P and R branches too weak to observe)

The correlation of the unknown compounds found in the present study with previously reported sulfur-nitrogen-fluorine compounds is hazardous since the field of nitrogen-sulfur-fluorine chemistry is as yet somewhat confused. Most of the basis for the identification comes from the chemical evidence presented by the original synthesizer, Glemser, who has since recanted some of his earlier statements (55).

On the basis of band intensity, compound B and then compound A appear to be the most abundant products of the fluorination of N_4S_4. Compound A is relatively unstable, decomposing or reacting to give compound C. The PR separation of 26 cm^{-1} of the 644 cm^{-1} band implies a relatively low molecular weight. These observations correspond to the characteristics of SNF as given by Glemser (26). In addition Glemser's spectrum of SNF (Figure II-2) shows a band at about 1375 cm^{-1}, the same position found for a band in the spectra examined in the present work. Glemser's spectrum however, must be looked at carefully.

The 1375 cm^{-1} frequency is presumed to correspond to the N-S stretching mode. In the compounds $RN{=}SF_2$ this mode is said to appear in the 1300-1400 cm^{-1} region (54). The assignment is thus quite reasonable. This leaves the 644 cm^{-1} band as the N-F stretching frequency. This is quite low considering that this vibration occurs at 905 and 1032 cm^{-1} in NF_3 (63), at 989 cm^{-1} in trans-N_2F_2 (62), at 766 cm^{-1} in ONF (64), and between 930 and 1025 cm^{-1} in N_2F_4 (36).

Compound B is the predominant product of the fluorination of N_4S_4. According to Glemser this is SN_2F_2. On the basis of preliminary investigations by NMR and mass spectroscopy Piper asserts that the product is actually NSF_3 (53). Two structures may be written for this compound $FN{=}SF_2$, in analogy with the organoiminosulfur difluorides, and $N{\equiv}SF_3$. The first structure corresponds to a derivative of SF_4, a very reactive compound while the second corresponds to a derivative of SF_6, a very unreactive compound. Since compound B neither decomposed on pyrolysis nor could be further fluorinated the indication is that it is actually NSF_3 with the second structure. This seems to agree with Piper's conclusions. Glemser has prepared NSF_3 and found that it did not react readily with water (28), whereas the organoiminosulfur difluorides are easily decomposed by water (54). This comparison implies that Glemser's NSF_3 is the same as the compound B prepared in the present investigation.

On the basis of the $N{\equiv}SF_3$ structure it is now possible to assign the frequencies 774, 819, 520, and 1625 cm^{-1} to the various modes. The 1625 cm^{-1} band is presumably the overtone of the most intense band at 819 cm^{-1}

since it is observable only at higher pressures. The S-F stretching frequencies of the compounds SF_4, SOF_2, SOF_4, and SO_2F_2 lie in the range 728-889 cm^{-1} (66, 69, 44, 70, 71) so that the assignment of the 774 and 819 cm^{-1} frequencies to S-F stretching modes is reasonable. The 1520 cm^{-1} frequency is assigned to the N-S stretching frequency because in SNF the N-S stretching frequency is 1375 cm^{-1} and this is for an approximate double bond. In NSF_3 the N-S bond is formally a triple bond and the stretching frequency should be higher. From his NMR data Piper asserts that all the fluorines are equivalent in this molecule. This would predict that NSF_3 is a symmetrical rotor. Two of the stretching vibrations would give rise to parallel bands and one to a perpendicular band. The parallel bands will have well-defined P, Q, and R branches whereas the appearance of the perpendicular band is not exactly predictable since it depends somewhat on the unknown angular momentum associated with a doubly degenerate vibration. Since the NSF_3 molecule probably does not deviate greatly from a spherical rotor it might be expected to have a central maximum but one which may be less sharply collected than the Q branch of a parallel band. Since the ^RP and ^PP branches of the successive subbands may be nearly superimposed, as likewise the ^RR and ^PR branches, the central maximum could be flanked by two subsidiary maxima, though these may well merge with the central peak (80). These predictions fit the observed band contours of NSF_3. The 774 and 1520 cm^{-1} bands have well defined P, Q, and R branches while the 819 cm^{-1} band is unresolved. The 819 cm^{-1} band is assigned to the degenerate asymmetric S-F stretching vibration and the 774 cm^{-1} band is the symmetric S-F stretch.

The parallel bands at 774 and 1520 cm^{-1} were found to have double Q branches. The 774 cm^{-1} band has a weaker Q branch at 778 cm^{-1}; the 1520 cm^{-1} band has its second Q branch at 1517 cm^{-1} which is not much weaker than the more intense Q branch. The simplest explanation for the presence of these additional Q branches is that they are the Q branches of hot bands. The hot band at 778 cm^{-1} is not an unreasonable explanation even though it lies on the high frequency side of the main band. The intensity of the hot band relative to the main band indicates that the population in an excited state is not large.

On the other hand the hot band at 1517 cm^{-1} is almost as intense as the main Q branch indicating a large population in an excited state. That an excited state might be significantly populated is suggested in a report of the microwave spectrum of NSF_3 (55). A satellite line is found which indicates a frequency of approximately 250 cm^{-1} for one of the bending modes. Such a vibration would have 0.86 as many molecules in the first excited state as in the ground state. This would be quite enough to produce the intense hot band at 1517 cm^{-1}.

Unfortunately the pure compound D could not be prepared in large quantities so that a definite conclusion as to its nature cannot be made. Compound D was a product of the pyrolysis of fraction IIIA which contained principally compounds A and B. According to Glemser this pyrolysis produces NSF_3 and NSF from SN_2F_2 and SNF. As has been pointed out there appears to be no SN_2F_2 in my preparations, and some of the SNF appeared to survive the pyrolysis. Two unidentified bands appeared in the spectrum of the pyrolysis product. They can be seen at 1160 and 1340 cm^{-1} in Plate XIII. Actually these bands had been observed before at much weaker intensity in Plate VIII. These could belong to NSF by the following reasoning. Glemser found that physical properties of his NSF to be similar to those of SO_2 with which it is isoelectronic (27). The two stretching vibrations of SO_2 are at 1150 and 1360 cm^{-1} with the latter, the asymmetric mode, being much more intense than the former (72). The same intensity relationship exists between the 1340 and 1160 cm^{-1} bands of compound D with the former being the more intense. The band types for NSF should be A for the asymmetric mode and an A, B hybrid with predominantly A character for the symmetric mode. The 1160 cm^{-1} band has a distinct Q branch which could satisfy this requirement. The bending mode in SO_2 has a frequency of 518 cm^{-1}. Compound D was not observed in the potassium bromide region so that its bending frequency is unknown and no comparison can be made.

b. Comparison of spectrum of compound A with Glemser's SNF.

The spectrum of SNF as reported by Glemser, Rogowski, and Richert appears to be identical with that of compound A reported here within their limited spectral range, but seems quite inconsistent with the structure they deduce from the electron diffraction study (52). There is a band at about 1375 cm^{-1} and a rising absorption at the low frequency end where their spectrum terminates at 650 cm^{-1}. The latter appears to be the edge of the 644 cm^{-1} band of SNF. The 1375 cm^{-1} band in Figure II-2 shows two distinct branches. The frequency mentioned corresponds to the N-S stretching mode. On the basis of the assumption that the SNF bond angle is 110°-120° the change in the dipole moment during the N-S stretch should lie relatively close to the axis of the smallest moment of inertia. The band should be an A, B hybrid with predominantly A character (81). Plate X shows the spectrum of a sample of gas with approximately 10mm of SNF. The 1375 cm^{-1} band shown has a distinct Q branch. The band of SNF shown in Figure II-2 therefore cannot be of the B type as appears at first glance. The most probable explanation is that the pressure was so high (50mm) and the resolution in this small reproduction is so low that the Q branch cannot be observed. Glemser was able to get a pressure of 50mm of SNF in his cell (of unknown length) while only about 4mm of relatively pure SNF and perhaps as much as 15mm of SNF in some of the mixtures was obtained in the present work.

A complete force constant analysis of SNF cannot be carried out as the frequency of the bending mode is unknown. An approximate analysis can be made if the frequency of this mode is sufficiently small. The spectrum of a mixture containing SNF was examined on a Perkin-Elmer Model 21 infrared spectrometer with a KBr prism and it was observed that there was no other band of SNF above 450 cm^{-1} since no band in that region examined decreased at the same rate as the 644 cm^{-1} band. There is the possibility that the 390 cm^{-1} band observed by Gallup and Koenig is the bending frequency but this cannot be said with certainty.

c. Estimation of force constants, bond distances, and bond numbers.

The separation of the bending mode is helpful in that the elements of the G matrix related to the bending mode require a knowledge of the bond distances. The only data on these quantities are those of Glemser and they are suspect.

The abbreviated G matrix for the SNF stretching modes is given below

$$G_{SNF} = \begin{vmatrix} .1028 & -.0358 \\ -.0358 & .124 \end{vmatrix}$$

where the masses are in atomic mass units. The GF matrix was obtained using a diagonal force constant F matrix in which the interaction constants are assumed to be zero. The numerical values of the force constants are in millidynes per Angstrom. The resulting secular equation is

$$\begin{vmatrix} .1028k_1-\lambda & -.0358k_2 \\ -.0358k_1 & .124k_2-\lambda \end{vmatrix} = 0$$

This secular equation was expanded and two simultaneous quadratic equations were obtained by substituting the observed values of

$$\lambda = \frac{4\pi^2 c^2 \nu^2_{cm^{-1}}}{10^5 N}$$

where $\nu_{cm^{-1}}$ is the observed frequency in reciprocal centimeters, c is the velocity of light in cm/sec, and N is Avogadro's number, 6.02×10^{23}. For $\nu = 1375$ cm^{-1}, $\lambda = 1.114$ and for $\nu = 644$ cm^{-1}, $\lambda = 0.2435$. k_1 was eliminated from the two equations to give a single equation quadratic in k_2. The solutions for k_2 are found to be 8.7 and 2.3 millidynes/A. Substituting these values into the other equation yields the corresponding values of k_1, = 2.7 and 10.4 millidynes/A. Of these alternatives the set $k_1 = 10.4$ and $k_2 = 2.3$ millidynes/A is more probable as the N=S stretching mode associated with the k_1 force constant would be expected to be larger than k_2.

Badger's rule can now be applied to these force constants to obtain a rough estimate of the bond distances (83).

$$(k_{NS})^{-1/3} = 1.87(D_{NS} - 0.94)$$
$$(k_{NF})^{-1/3} = 1.75(D_{NF} - 0.68)$$

where the k's are in megadynes/cm and the distances are in angstroms. The N-S bond distance is calculated to be 1.47A and the N-F bond distance is calculated to be 1.61. These values differ considerably from the sums of the normal single bond covalent radii. For an N-S double bond the distance should be 1.58A and for a normal N-F single bond the distance should be 1.38A. Pauling's relationships are now used to calculate the bond numbers for the bonds in SNF (84).

$$D_{NS}(n') = D_{NS}(1) - 0.711 \log n'$$
$$D_{NF}(n) = D_{NF}(1) - 0.601 \log n$$

For the N-S bond n' is found to be 2.34 and for the N-F bond n equals

0.42. The sum of these is less than the value of three which would be expected for the valence of nitrogen. However the discrepancy is not surprising considering the approximations that were involved in the calculations.

Using the above bond distances and assumed bond angle of 120° the moments of inertia of SNF were calculated. The two principal moments of inertia in the plane of the molecule are 117×10^{-40} and 37.7×10^{-40} g-cm^2. Although SNF is an asymmetric rotor the symmetric rotor formula will be used to approximate the PR separation of the bands. The asymmetric rotor band envelopes for molecules with $\rho > 5/4$ and $S < -1/2$ have not been calculated by Badger and Zumwalt (81). For SNF $\rho = 2.25$ and $S = -0.8$. Gerhardt and Denison's (80)formula for the PR separation of parallel bands is

$$\Delta \nu_{PR} = \frac{s(\beta)}{\pi}\left(\frac{kT}{I_A}\right)^{1/2}$$

where $s(\beta)$ is a function of β which is $(I_A/I_B)-1$. For SNF, β =is 2.59 and $s(\beta)$ is 1.22. $\Delta \nu_{PR}$ is the PR separation in sec^{-1}, k is the Boltzmann constant, T is the absolute temperature and I_A is the non-unique moment of inertia. $\Delta \nu_{cm^{-1}}$ is calculated to be 22.7 cm^{-1} and in the 644 cm^{-1} band of SNF is observed to be 26 cm^{-1}. This disagreement is not serious since the formula is only approximately applicable.

An exact force constant calculation for NSF_3 cannot be carried out since the bending frequencies are unknown. An approximation to the force constants may be made by assuming that the N-S and S-F vibrations are independent. The approximation of each bond stretching mode as a diatomic harmonic oscillator yields $k_{NS}=13.4$ millidynes/A and for k_{SF}, 4.5 millidynes/A. This S-F force constant is somewhat higher than the k_{SF} in SF_6 which is 3.55 (85).

These values are substituted in Badger's rule to give approximate bond distances. The result gives 1.42A for the N-S bond and 1.64 for the S-F bond. These are the expected values for the N-S triple bond and for the S-F single bond. The bond numbers are obviously three and one respectively for these bonds, and pleasantly enough they add up to six, the oxidation number of the sulfur in this molecule.

The moment of inertial of NSF_3 can be estimated using these bond distances and an assumed FSF bond angle. The bond angle will be taken as 97° as that is the value for the FSF angle in SO_2F_2 (86). The values obtained were 192 g-cm^2 for the moment about the figure axis and 200 g-cm^2 for the moment perpendicular to the axis. Applying the equation for the PR separation cited above leads to the predicted value of 22 cm^{-1} for parallel bands. The separation of the 774 cm^{-1} band is 27 cm^{-1} as shown in Plate XV while the PR separation for the 1520 cm^{-1} band is somewhat inaccurate as only the R branch is well separated from the Q branch which is double and because an inverse water band lies close to the peak of the R branch. These conditions make the estimate of the position of the maximum uncertain. Depending on this estimate the PR separation of this band is 22-26 cm^{-1}. The agreement with the calculate value is quite poor. The agreement might be improved if the S-F distance were shortened. Shorter S-F distances are found in SO_2F_2, 1.53A (86) and in SF_6, 1.56A (87). Since a complete normal coordinate treatment was not possible no definite conclusions may be drawn.

A preliminary report of the microwave spectrum of NSF_3 (55) indicates that the structure is

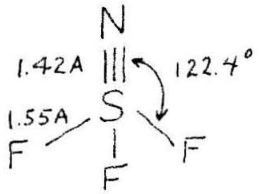


Plate XV. 774 cm^{-1} band at high resolution

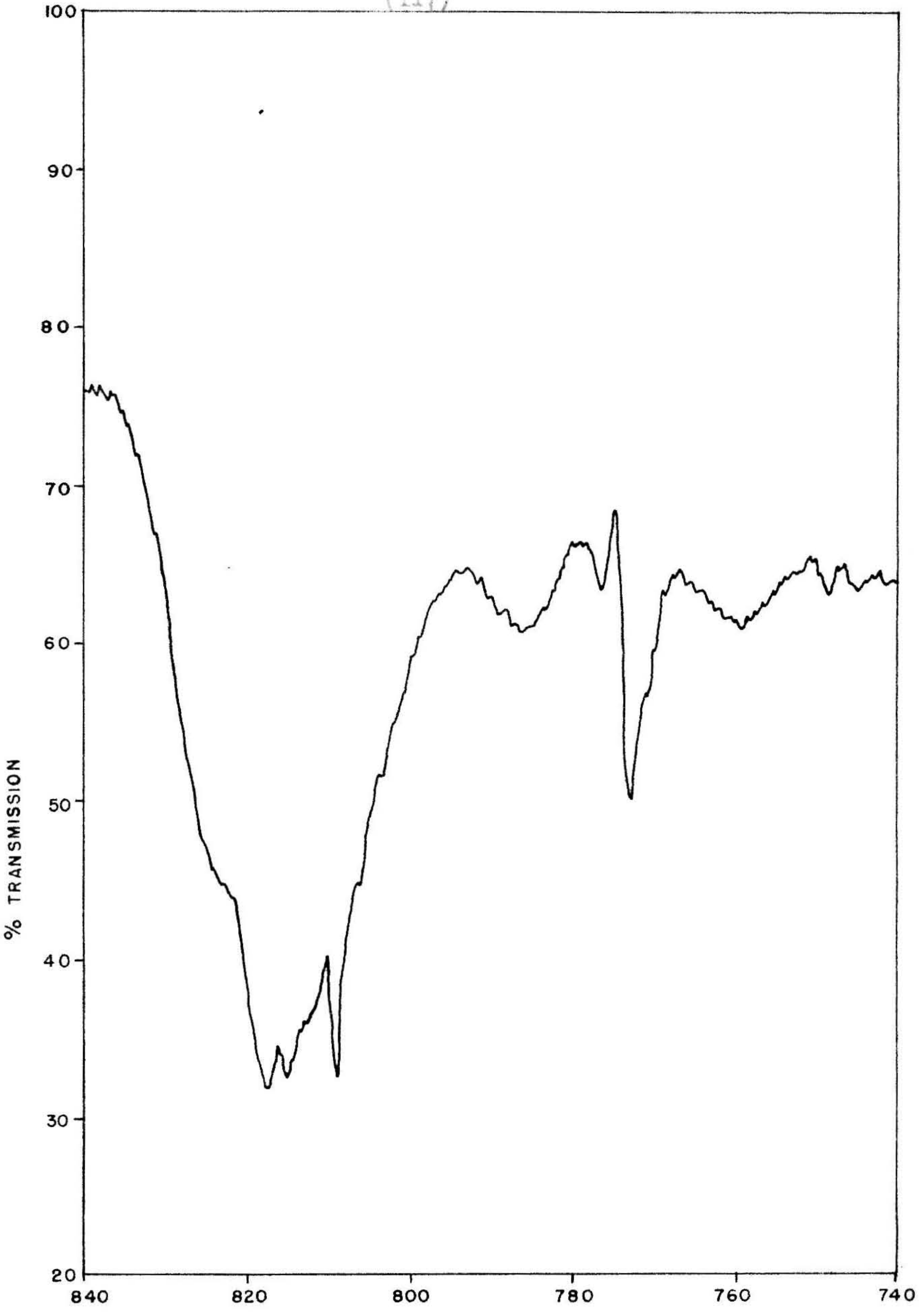

100
90
80
70
60
50
40
30
20
% TRANSMISSION
840
820
800
780
760
740
WAVE NUMBERS

Plate XV.

The shorter S-F distance would be sufficient to bring the observed and calculated PR separations into good agreement. That the bond distances used in the rough estimation of the moment of inertia are inaccurate is to be expected as they were derived from the very crude approximation of independent vibrations.

Compound D was taken to be NSF on the information given by Glemser. He said that NSF was prepared by pyrolysis of the compounds SN_2F_2 and SNF. An increase was found in the amount of D present when NSF_3 in the mixtures prepared during this investigation was pyrolyzed. Glemser found the physical properties of NSF to be similar to those of SO_2 with which it is isoelectronic. If the physical properties of NSF paralleled the properties of SO_2 it was surmised that perhaps the vibrational spectrum should also be similar to the spectrum of SO_2. The two bands of D were found at 1160 and 1340 cm^{-1} while SO_2 has its bands at 1150 and 1360 cm^{-1}. The relative intensities of the two bands of D were the same as the corresponding bands of SO_2. On these bases it was considered that compound D was probably NSF.

The abbreviated G matrix for NSF was calculated for NSF using an assumed bond angle of 120° and separating out the bending mode as was done with SNF.

$$G_{NSF} = \begin{vmatrix} 1028 & -.0157 \\ -.0157 & .0838 \end{vmatrix}$$

After setting up the GF matrix the secular equation was solved as in the case of SNF. The solutions were $k_1 = 9.9$ and 8.1 millidynes/A and $k_2 = 9.9$ and 12.1 millidynes/A.

These values are quite unreasonable. No matter which set is chosen the S-F force constant is much greater than the value for NSF_3 and SF_6.

The values correspond to S-F bond numbers considerably in excess of one, a result which is much beyond believability. The N-S force constant corresponds to a bond number of 2.30. The above result indicates that the structure

$$:\overset{-}{\ddot{N}} = \ddot{S} = \overset{+}{\ddot{F}}:$$

contributes to the resonance hybrid to a large extent. However, fluorine is so electonegative that it does not seem possible that such a structure would be a stable configuration. This consideration leaves it very much in doubt as to whether compound D is in reality NSF.

VI. A reexamination of the infrared spectra of N_4S_4 and $N_4S_4H_4$.

a. Introduction.

The infrared spectra of N_4S_4 and $N_4S_4H_4$ have been investigated by Lippincott and Tobin (50). At that time they had available two conflicting determinations of the structure of N_4S_4 which were based on two dimensional projections (88, 89). They were attempting to decide between the two possibilities on the basis of the observed infrared and Raman spectra. They assigned the bands of N_4S_4 on the basis of a cage structure with the nitrogens at the corners of a tetrahedron which interpenetrated the square of sulfurs. However a recent redetermination of the structure of N_4S_4 shows that the positions of the nitrogens and sulfurs are the reverse of the structure suggested by Lippincott and Tobin. This new determination was obtained from three dimensional Fourier maps which yield more accurate parameters than the earlier two dimensional projections (79). Lippincott and Tobin believed that $N_4S_4H_4$ had a structure similar to N_4S_4 since the spectra of the two compounds were regarded by them as being very similar. As shown below this is an unwarranted assumption. The structure of $N_4S_4H_4$ as determined by x-ray diffraction (90) shows that it is really a pseudosulfur, i.e., every other sulfur in the S_8 ring is replaced by an NH group to give $S_4\ (NH)_4$.

b. Preparation and identification of $N_4S_4H_4$.

The preparation of N_4S_4 has been described earlier. $N_4S_4H_4$ was prepared by the method of Meuwsen (91) by reducing N_4S_4 with stannous chloride in ethanol. The $N_4S_4H_4$ was extracted with pyridine from the solid mixture obtained on evaporating the ethanol. The product was a white powder which over a period of time gradually turned pale yellow. To allay fears that the product might not be $N_4S_4H_4$ an x-ray powder pattern was taken. The positions of the observed lines agreed precisely with the positions calculated from the known dimensions of the orthorhombic unit cell. Another check was given by a known sample of $N_4S_4H_4$ kindly provided by Doctor H. Spiesecke of Harvard University. It gave the same powder pattern as the material synthesized by the investigator.

c. Observed frequencies of N_4S_4 and $N_4S_4H_4$.

The spectra of N_4S_4 and $N_4S_4H_4$ in pressed KBr discs were obtained on a Perkin-Elmer Model 21 spectrophotometer. The observed frequencies are given in Table I along with the data of Lippincott and Tobin.

Table I

Infrared Frequencies of N_4S_4 and $N_4S_4H_4$

N_4S_4				$N_4S_4H_4$			
Present work		Reference (50)		Present work		Reference (50)	
396 cm^{-1}	s	397 cm^{-1}	w	406 cm^{-1}	w	407 cm^{-1}	m
416	m	412	w	460	m	462	s
453	w	460		520	m	516	m
470	w			540	m	541	m
519	m	519	m	(above two bands poorly resolved)			
		531					
550	vs	552	s				
		557	s				
700	vs	696	s	699	w	693	w
726	s	719	s	712	w	705	w

Table I (continued)

N_4S_4				$N_4S_4H_4$			
Present work		Reference (50)		Present work		Reference (50)	
928	vs	925	s	830	vs	780	s
1380	w			1295	m	1262	w
						1296	w
						1302	s
				3205	s	3220	s
				3280	s	3280	s
						3320	m

w = weak; m = medium; s = strong; vs = very strong

d. Discussion.

The major difference between the results is the position of the main band of $N_4S_4H_4$. Lippincott and Tobin reported it at 780 cm^{-1} whereas it was found to be at 830 cm^{-1}. Curiously it happens that they had published an earlier note in which they reported this band at 828 cm^{-1} (92). This odd contradiction may have been caused by their misreading the scale of their spectrum although it seems an absurd mistake to make.

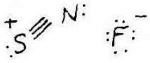
The N-H bending vibration at 1295 cm^{-1} was found to be a single sharp band but in Lippincott and Tobin's work three overlapping bands were found in this region. For the N-H stretching modes two sharp bands were found at 3205 and 3280 cm^{-1} which correspond to the 3220 and 3285 cm^{-1} bands as found by Lippincott and Tobin. In addition they report another weak band at 3320 cm^{-1}. The C_{4v} symmetry of $N_4S_4H_4$ predicts that there should be only two infrared active N-H stretching frequencies and only one infrared active frequency for N-H bending in the plane of the hydrogen atoms. These numbers of the predicted frequencies agree with those found in the present work.

The additional bands found by Lippincott and Tobin might be explained on the basis of impurities. It may have been possible that they had some

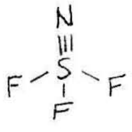
S_7NH present in their sample of $N_4S_4H_4$. This pseudosulfur is a byproduct of the synthesis of N_4S_4 (93). If they had used relatively impure N_4S_4 to prepare $N_4S_4H_4$ the S_7NH would be carried along with the $N_4S_4H_4$. They do not state whether purified N_4S_4 was used or not.

VII. Summary.

The nitrogen-sulfur-fluorine compounds examined in the present investigation were prepared by fluorination of N_4S_4 by AgF_2. The gaseous products were partially purified by bulb to bulb fractionation under reduced pressure. The infrared spectra of several preparations were determined. Known compounds found as impurities were CCl_4, $CFCl_3$, SO_2, SF_4, SF_6, SOF_2, SO_2F_2, and SiF_4. The bands observed in the NaCl region by Gallup and Koenig were those found by the present investigation to be mainly impurities. Bands believed to belong to new compounds were found at 644, 758, 774, 819, 907, 1160, 1257, 1340, 1375, 1520, and 1625 cm^{-1}. These bands were assigned to four compounds on the basis of their changes in intensity as a function to time or of their intensities in various fractions.

Compound A had two bands at 644 and 1375 cm^{-1} which decreased with time. This compound was assigned to SNF because of its instability and because it is a product of the original synthesis. The spectrum is in agreement with the one found by Glemser for pure SNF (52). From the approximate force constants the bond distances were estimated to be $d_{NS}=1.47A$ and $d_{NF}=1.61A$ representing bond numbers 2.3 and 0.42 respectively. These values indicate that  is a better representation of the actual structure of the molecule than the completely covalent structure. These distances were found to be reasonably consistent with the observed PR separation of the 644 cm^{-1} band.

Compound B was the main new product of the fluorination. It was not decomposed by heating at 250°C for 60 hours, and could not be further fluorinated. This chemical behavior was used to conclude that the compound was NSF_3. In the NaCl region this compound had three strong bands at 774, 819, 1520 cm^{-1} and a weak band at 1625 cm^{-1} which was considered to be the overtone of the 819 cm^{-1} frequency. The band envelopes of the three strong bands correspond to those expected for a symmetrical rotor. The 774 and 1520 cm^{-1} bands have well defined Q and R branches with the 774 cm^{-1} band also having a sharp P branch. The 819 cm^{-1} band could not be resolved. This set of band envelopes fits the requirements of the symmetrical rotor which would have two parallel bands and one perpendicular band corresponding to the bond stretching modes. The 1520 cm^{-1} band is a parallel band corresponding to the N S stretching mode. The 819 cm^{-1} would therefore belong to the asymmetric S-F stretching mode and the 774 cm^{-1} band to the symmetric stretching mode. The approximate force constants and band contours were found to be consistent with the structure



as suggested by the results of the NMR investigation (53).

Compound C is still unknown. It is the product of a reaction of SNF. It has three bands at 758, 907, and 1257 cm^{-1} all having Q branches with the latter two having well-defined P and R branches, with PR separations of 26 cm^{-1}. It was conjectured that compound C might be $FN=SF_2$ on the basis of reasonable assumptions of the 1257 cm^{-1} frequency as an N=S stretch, the 907 cm^{-1} frequency as an N-F stretch, and the 758 cm^{-1} frequency as an S-F stretch. Unfortunately this structure is not too probable as the observed PR separations are much larger than would be expected for a molecule of such a molecular weight and mass distribution. The nature of compound C is still open to investigation.

Compound D which has two bands at 1160 and 1340 cm^{-1} was originally believed to be NSF but the approximate force constant analysis leads to unreasonable values. This could conceivably result from the neglect of a significant interaction constant but it is more likely that D is an unknown impurity not contained in the table of possible contaminants.

Glemser stated that $SO_3^{=}$ was formed upon alkaline hydrolysis of all of his compounds, SN_2F_2, SNF, SNF_3, and NSF. The present study has found no evidence for the existence of SN_2F_2 and the structure of NSF_3 shows it to contain sulfur in the +6 state. What Glemser thought to be SN_2F_2 was actually a complex mixture of many compounds as was found in the present investigation. It appears that on hydrolysis the SO_2, SOF_2, SF_4, and SNF present in these mixtures formed $SO_3^{=}$ which deceived him into thinking that he had a new compound with sulfur in the +4 state. He did his sulfur content analysis of the hydrolysis products by oxidizing all the species of sulfur present to $SO_4^{=}$. If any $SO_4^{=}$ was present before the oxidation it would not have been detected by acidification of the solution as is SO_3^{--} but it would be included in the total sulfur found by analysis. NSF_3 should form $SO_4^{=}$ on hydrolysis but no $SO_3^{=}$. Evidently the original sample Glemser had prepared of this compound contained some SO_2 and SOF_2 present as impurities which gave rise to the $SO_3^{=}$ he detected in the hydrolysis products. In his recent paper he admitted the presence of SOF_2 in his first preparation of NSF_3. That SOF_2 should have been present is not surprising since the difference in boiling points is only 17°C which would make it difficult to separate completely these two compounds by bulb to bulb fractionation as was done originally (28).

The infrared spectra of N_4S_4 and $N_4S_4H_4$ were reexamined in order to resolve the conflict between an earlier infrared investigation and the known structures of these compounds. The identity of the $N_4S_4H_4$ used to obtain the spectrum was checked by an x-ray powder pattern. The spectrum of N_4S_4 agreed with the previously published spectrum. In contrast the spectrum of $N_4S_4H_4$ showed several differences. The band reported at 780 cm^{-1} was found to lie at 830 cm^{-1}, and several bands previously reported were found to be missing. The number of N-H frequencies observed was found to agree with the number predicted by the C_{4v} symmetry of the molecule. It was suggested that the additional bands reported by Lippincott and Tobin were caused by S_7NH.

VIII. Addendum.

After the foregoing experimental work and its interpretation was completed two papers by Glemser and Richert appeared giving an improved synthesis and separation of SNF and SNF_3 and presenting the infrared and NMR spectra of these compounds (94, 95). Their results of the infrared spectra are in agreement with those found in the present investigation. Their new spectrum of SNF shows the 1375 cm^{-1} band to have a Q branch. It appears that faulty reproduction of their earlier spectrum was the cause of the failure to see the Q branch of the band in Figure II-2. In extending their spectral range they located the bending frequency of SNF at 366 cm^{-1}. They reported force constants for the N-S and N-F bonds as 10.4 and 1.5 millidynes/A respectively and a bending force constant of 0.6 millidynes/A. However, these were based on the bond distances as determined by Rogowski (96) by electron diffraction. The paper by Rogowski has recently been published and it appears that he did not attempt any trial structures with a short N-S distance and a long N-F distance. Lack of time prevented this investigator from calculating the diffraction curve for the model that would be in agreement with the infrared spectrum. The question remains open as to whether the diffraction curve calculated for  would agree with the observed diffraction curve.

A calculation of the force constants for SNF using the N-S distance of

1.47A, an **N-F** distance of 1.61A and an assumed angle of 120° and now including the bending force constant yields k_{NS}=10.4, k_{NF}=1.7, and k_{SNF}=0.45 millidynes/A. The **N-F** force constant is now even lower than the value found in the approximate treatment. That it should be weaker than the k_{NF} in ONF (2.4 millidynes/A) (97) is not surprising, but the 30% drop is unexpected. It would appear that there is only 0.27 bond between the nitrogen and the fluorine, a value which is only half of the **N-F** bond in ONF. The low force constant may be the result of neglecting the interaction constants in the **F** matrix. If these interaction constants were known and were included in the calculation the **N-F** force constant might be increased somewhat. Nevertheless the **N-F** bond is the weakest ever encountered.

For NSF_3 Glemser and Richert found the same bands in the NaCl region as were found in the present investigation. Their assignments of these bands were also the same. They extended the range of frequencies covered to the KBr and CsBr regions where they found three bands at 521, 429, and 332 cm^{-1}. All of these bands had easily distinguishable P, Q, and R branches. Two of these three bending modes would be expected to be doubly degenerate and to have unresolvable band envelopes like the 819 cm^{-1} band. However as was pointed out previously the possibility exists that the sub-bands may be superimposed in such a way that all the Q branches lie on top of one another. The P, Q, and R branches then would all occur in the same place and not produce a broad band. Such a case exists in the 493 cm^{-1} bending mode of NF_3 (63).

Glemser and Richert found that on addition of H_2O vapor to SNF in a gas cell a large amount of SO_2 was formed (94). Also they found in the spectrum of this mixture the bands of what has herein been called compound C. They identify this material with SONH which they had investigated earlier in greater detail though the details have not yet been published.

They show on the same reproduction the spectrum of pure SONH (source unknown) which has strong bands at 1260, 910, and 760 cm^{-1}. Weak bands were found at 3370 and 1090 cm^{-1}. The 760 cm^{-1} band has a very intense Q branch while the 1260, 1090, and 910 cm^{-1} bands have Q branches that have approximately the same peak absorption as their P and R branches. The 3370 cm^{-1} band appeared to have only P and R branches.

The reactions that lead to SONH and SO_2 are

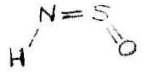
$$SNF + H_2O = SONH + HF$$

$$SONH + H_2O = SO_2 + NH_3$$

There were no bands of HF or NH_3 present in the spectrum, nor were there any bands of NH_4F which would result from the combination of the HF and NH_3. It may be that the layer of NH_4F that condenses on the windows of the cell is not sufficiently thick to produce any noticeable absorption.

The frequencies of this compound may be assigned as follows on the basis of the thionylimide structure, O=S=NH. This molecule is isoelectronic with SO_2 and therefore would be expected to be planar. Like SO_2 it is an asymmetric rotor with the B axis almost bisecting the NSO angle, the A axis perpendicular to B in the plane, and the C axis perpendicular to the plane.

The 760 cm^{-1} band has very strong Q branch which indicates that it is a C type band. The out of plane bend of the hydrogen would be of this character. In secondary amides this mode is found at 700 cm^{-1} (98) so the assignment of the 760 cm^{-1} band is reasonable.

The 3370 cm^{-1} corresponds to the N-H stretch. The band envelope is of the B type with only P and R branches. This type of band would be expected only if the structure had the hydrogen cis to the oxygen  .

The N-H bond direction was calculated to be within 5° of the B axis. If the hydrogen were trans the N-H direction would almost be parallel with the

A axis and the stretching mode would give rise to an A type band.

There remains three bands to assign. The four remaining modes are the N=S and S=O stretches or perhaps more precisely the symmetric and asymmetric N=S=O stretching modes, and the NSO and HNS angle bending modes. the NSO bending vibration should not be much different from the angle bending mode in SO_2 which lies at 518 cm^{-1} (72). The region of this vibration was not examined so any further statement concerning this mode cannot be made. In O=NH the bending mode lies at 1150 cm^{-1} (99) and this suggests that the 1090 cm^{-1} frequency probably belongs to the HNS bending mode. This band is of the A type as shown by its PQR structure. The A character for this band is expected if the molecule is in the cis configuration. This agrees with the conclusion drawn from the nature of the envelope of the 3370 cm^{-1} band.

The two remaining bands at 1260 cm^{-1} and 910 cm^{-1} are by elimination assigned to the stretching modes of the NSO group. The 910 cm^{-1} frequency seems to be rather low for a structure so similar to SO_2. However in the absence of additional information no further comment may be made.

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PROPOSITIONS

> "Scientists who are always afraid
> of being wrong, some way or other
> never manage to be really right."
>
> Ernest A. Hooten

Proposition I. A relationship between bond dissociation energies and boiling points of compounds is suggested. The relationship is used to decide between conflicting values of the N-N bond dissociation energy and to predict the possible existence of new compounds.

The bond energies derived from thermochemical data do not represent the energy required to break a given bond in a polyatomic molecule. That energy is properly the bond dissociation energy. A knowledge of these dissociation energies is necessary in order to explain or predict the mechanism or kinetics of a reaction. Much data on bond dissociation energies has recently become available through electron impact studies of the appearance potientials of molecules in the mass spectrometer. Also estimates of activation energies in decomposition studies are useful (1).

It would be desirable to have a simple relationship between bond dissociation energy and a more easily measured quantity. The following exposition suggests such a relationship.

Errede has suggested a simple empirical relationship to calculate bond dissociation energies (2). It is

$$D\ (\text{K cal / mole}) = \alpha \epsilon_1\ \epsilon_2$$

where α is a scale factor and the ϵ 's are parameters characteristic of the atoms or groups connected by the bond. For bonds to carbon α

was chosen as 71 kcal/mole in order to make the ϵ 's near unity. The calculated values agree with the experimental values within 1-2 kcal/mole in 80% of the compounds investigated.

It appeared that the values of Errede's ϵ's for the non-common groups in a series of compounds with a common group followed the trend of the boiling points of the compounds. The relationship was

$$T_v \sqrt{\epsilon_2} = C_1$$

where T_v is the vaporization temperature in °A; ϵ_2 is the Errede parameter for the non-common group, and C_1 is a constant characteristic of the common group. As an example take the series of methyl compounds:

Compound	T_v	$\sqrt{\epsilon_2}$	$T_v \sqrt{\epsilon_2}$
CH_3F	194	1.22	236
CH_3Cl	249	1.02	254
CH_3Br	277	0.93	257
CH_3I	316	0.83	260
CH_3CF_3	226	1.08	244
CH_3NO_2	374	0.75	282
CH_3CN	351	1.13	397
CH_3CCl_3	347	0.97	337

or for ethyl compounds

C_2H_5-F	235	1.22	287
-Cl	283	1.02	289
-Br	311	0.93	289
-I	345	0.83	286
$-CF_3$	261	1.08	283
$-NO_2$	388	0.75	291
-CN	360	1.13	412

When the common group is F the Cl, CH_3-, C_2H_5-, and CCl_3 compounds do not give the $T_v\sqrt{\epsilon}$ product of approximately 157 as do CF_3-, NO_2-, and FO-. It appears that there is a dominance effect that the rule is obeyed when the compound is written as the derivative of the dominant group. The order of dominance was found to be $CCl_3 > CH_3 > C_2H_5 > Cl > F > CF_3 > NO_2$

It was found that none of the compounds containing the CN group obeyed this relationship. Two classes of compounds do not fit the relationship: First, those compounds such as alcohols, acids, nitriles, and aldehydes which can form hydrogen bonds and second, aromatic compounds. Among organic compounds the relationship works for derivatives of alkanes, olefins, acetylenes, and haloolefins.

One can conclude from the general types of compounds which obey the relationship and those that do not that the rule is reflected in compounds whose liquids are associated only by dipole-dipole interactions.

The usefulness of this relationship is limited in organic chemistry since so many compounds are excluded. However, there are many instances in inorganic chemistry where a knowledge of bond dissociation energies would be helpful and the data are lacking. It is at this point that the relationship is of some utility.

Consider the series of compounds containing the NF_2 group that have recently been prepared. They are HNF_2, $ClNF_2$, CH_3NF_2, $C_2H_5NF_2$, CF_3NF_2, NF_2NF_2, and the long known NF_3. The first of the series belongs to the hydrogen bonded class and should not follow the boiling point relationship. The methyl and ethyl compounds are used to calculate ϵ_{NF_2}, which is 0.99.

The boiling points of the remaining compounds are calculated and compared with the observed values.

Compound	$T_v\sqrt{\epsilon}$	T_v(calc.)	T_v(obs.)	$T_v\sqrt{\epsilon_{NF_2}}$
$F-NF_2$	157	158	158	194
$Cl-NF_2$	210	212	206	210
CF_3-NF_2	200	198	194	204
NF_2-NF_2	(203)	205	200	- -

$T_v\sqrt{\epsilon}$ for NF_2 is 203. The agreement between the observed and calculated boiling points is good.

There has been considerable controversy over the N-N bond dissociation energy in N_2F_4. The values reported are 19 kcal/mole, (3), 30 kcal/mole (4), and 54 kcal/mole (5). The boiling point relationship may be applied to give an estimate of this energy.

Errede found for the relation between N-X bond dissociation energies and the ϵ's was

$$D(\text{kcal/mole}) = 54\,\epsilon_1\epsilon_2$$

One example he did not use in deriving this relationship was N_2O_4. For NO_2- $\epsilon = 0.57$ which predicts that the N-N bond dissociation energy will be 17.6 kcal/mole. The observed value is 14 kcal/mole (6). For N_2F_4 this formula predicts $D(NF_2-NF_2) = 53$ kcal/mole, quite good agreement with reference (5). It may be that Errede chose the proportionality constant too high. Even better agreement is obtained for N_2O_4 and N_2H_4 if the scale factor is taken as 50 kcal/mole. This value now makes the agreement for the N-Cl energy in NO_2Cl excellent; D(calc.)=29.6 kcal/mole, D(obs.)=29.5 kcal/mole (7).

A check on the value of ϵ_{NF_2} is available in the dissociation energy of NF_3. From the equation

$$D = 50\ \epsilon_{NF_2}\ \epsilon_F$$

the calculated value is 75 kcal/mole compared to the observed value of

74 kcal/mole (8).

From the boiling point rule the following ϵ's were obtained

Group	ϵ
NF_2	1.00
OF	1.23
SO_2X	$0.33\,\epsilon_x$
SF_5	0.64
COF	0.85
COCl	0.69
SCF_3	0.59

The following values of $T_v\sqrt{\epsilon}$ for different groups were found

Group	$T_v\sqrt{\epsilon}$
F	157
CF_3	200
Cl	210
CH_3	250
NO	263
NO_2	263
CCl_3	360
NF_2	203
SF_5	263
$CH{=}CH_2$	270
$CF{=}CF_2$	250

For NH_2 and OH Errede gave the values of ϵ as 1.05 and 1.23 respectively. These are quite close to the values for NF_2 and OF. If the series were to continue to carbon ϵ_{CH_3} should be approximately equal to ϵ_{CF_3}; in actuality they are 1.08 and 1.15. This difference is reflected in the C-C bond dissociation energy of 65 kcal/mole for CF_3-CF_3 and 83 kcal/mole for CH_3-CH_3 (9).

The Errede relationship can be used to predict the dissociation energies of new compounds whose ϵ 's have been derived from the boiling point rule. Such a compound would be NF_2-NO. Since NO is dominant over NF_2 the boiling point relationship is

$$T_v = 263/\sqrt{\epsilon}_{NF_2}$$
$$T_v = 266$$

The predicted bond dissociation energy would be 37 kcal/mole. This would make the compound as stable as CF_3NO which has a calculated bond energy of 41 kcal/mole; CF_3NO does dimerize under certain conditions (10) but the monomer is stable. CF_3NO copolymerizes with CF_2=CF_2 to form elastomers (11). NF_2NO would be expected to undergo the same reaction. The synthesis of NF_2NO could be accomplished by merely mixing N_2F_4 and NO together and heating. FO-NO would be predicted to be stable but because the OF bond is weaker than the N-F bond it would rearrange to NO_2F. A similar exists with the unknown CH_3NO. If formed it instantly rearranges to CH_2=NOH.

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Proposition II. It is proposed that a solvent extraction procedure using tri-n-octylamine to separate zinc from aluminum be introduced into the freshman qualitative analysis scheme.

The students in freshman chemistry have done an experiment in quantitative analysis using a cation exchange resin. It would be desirable to utilize their previously gained knowledge of ion exchange phenomena in the qualitative analysis course. It is possible to use the method of extraction of anions by long-chain trialkyl amines (six or more carbons) since their action is analogous to the action of anion exchange resins (1). The extraction method has advantages over the anion exchange method in being quick, easy, and in the extractant having a larger capacity for the metal ions extracted.

Of the elements in the amphoteric group zinc is the only one whose extraction by long-chain tertiary amines had been extensively investigated (2). The distribution ratio shows the same HCl dependence as the absorption of zinc anions by an anion exchange resin (3). On the close analogy, the results of anion exchange investigations were used to decide that zinc can be separated from aluminum by extraction with tri-n-octylamine (TOA).

The following modification of Swift's qualitative analysis scheme (5) is proposed.

Carry out the solution of the carbonate precipitate of zinc and aluminum as given in the first paragraph of P. 74.

Separation of Zinc. Add to the solution containing the zinc and aluminum 5 ml of 5% solution of TOA in 1,2 dichlorobromoethane. Stopper the test tube and shake for 30 seconds. Allow the layers to separate. Remove the aqueous layer (upper) with a dropper and place it in another test tube.

Precipitation of aluminum. Add to the solution from the extraction procedure 3 ml of 3F NH_4OH. White ppt, presence of aluminum. Filter the ppt. Wash with 1ml of water and discard wash water. Treat the precipitate by P. 75.

Extraction of Zinc. To the test tube containing the organic layer add 3 ml of 6F NH_4OH. Stopper the test tube and shake for 30 seconds. Remove the aqueous layer with a dropper and place it in another test tube. Treat the solution by P. 76. Discard the organic layer into the bottle provided on the side shelf.

The modification is useful as a teaching device to show the use of a modern separation method. The students have seen in the ion exchange experiment how extraction occurs in the simple case of cations where only the coarse distinction between heavy metal ions and hydrogen ions is made. With TOA extraction the interplay of formation constants of anionic complexes and the relative ease of combination of these anions with the positive ions of the amine are demonstrated.

Both qualitative and quantitative problems can be based on this procedure.

From the chart given by Kraus and Nelson (4) the student could be asked to devise separations of elements other than zinc and aluminum. The variation of distribution ratios with HCl concentration and especially with the oxidation state of the element allows for numerous problems of this type.

More quantitative problems can be constructed by asking what per cent of an element which is partially extracted at a given HCl concentration remains in the aqueous phase after several extractions, or similarly how the separation of two elements can be improved by backwashing. Another problem, involving equilibria, would be to find the optimum HCl concentration for extraction when the formation constant of the extractable species is known and the value of the equilibrium constant for

$$AH^+ MCl_n^- + Cl^- \rightleftharpoons AH^+ \; Cl^- + MCl_n^-$$

is known.

A 5% by weight solution is prepared by dissolving TOA in 1,2-dichlorobromoethane, a non-inflammable solvent with good characteristics for the extraction (6). Five milliliters of this solution is sufficient to extract 40 mg of zinc. Since the extracting solution can be regenerated with base like an anion exchange resin it can be reused, spreading the original cost over a longer period of time.

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Proposition III. It is proposed that the viscosity of a dilute solution of an electrolyte as a function of temperature will go through a rapid change at a temperature lower than the hydration temperature of the pure compound when another electrolyte having the same anion in common is present.

It has been observed by Fujita that the viscosity of a 1% solution of Na_2CO_3 undergoes rapid changes in the vicinities of the hydrate transition temperatures (1). He reported that other investigators had found similar effects in the temperature dependence of conductivity and speed of ultrasonic waves in dilute solutions of sodium sulfate. Also Joshi and Joshi observed the transitions by following the refractive indices of solutions of Na_2SO_4 and $MgSO_4$ as a function of temperature (2). Their data is relatively poor in that the transition temperatures are poorly defined and spurious breaks appear in their curves probably because of inadequate temperature control. Nevertheless the effect does exist.

That such changes in the viscosity of saturated solutions occur at the hydrate transition temperature has been known for a long time (3). The effect has been utilized to determine these transition temperatures. It is surprising however, that it appears in dilute solutions that the solution knows what solid phase with which it would be in equilibrium if the solid phase were present. This would be true if the ions of the solute were in an environment that approximates the environment in the crystalline solid.

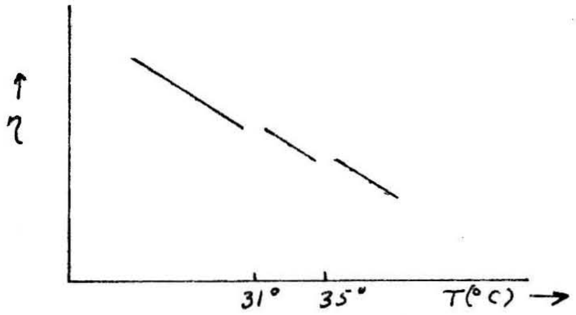
The concept that ions in aqueous solutions are hydrated is now well established. An equation for calculating activity coefficients that takes into account ionic hydration as well as interionic attraction has been proposed by Robinson and Stokes. The Robinson-Stokes relationship is

$$\log \gamma_{\pm} = \frac{-Az_1z_2\sqrt{I}}{1 + Ba\sqrt{I}} - \frac{h}{\nu}\log a_A - \log\left[1+0.001\ W_A\ (\nu-h)m\right]$$

where h is considered to be the hydration number of the compound and a is the radius of the hydration sphere (4). The hydration numbers calculated from this equation using known activity coefficients agree reasonably well with the values obtained from a modified Stokes' law for the viscosity of ionic solutions (5). They also note that the hydration number does not belong to the cation alone but depends on the nature of the anion as well.

The dependence of the hydration number on the anion is to be expected when one considers the change in the viscosity of a dilute solution at the hydrate transition temperature. If the anions had no effect the hydration shells of the cations of all salts with the same cation would be the same at a given temperature and the viscosity changes would occur at the same temperature or not at all. The latter situation describes a very dilute solution. In the case of 0.1F Na_2CO_3 the ions would be 17 Å apart, on the average. The force of the anions on the hydration shell is still quite strong at this distance since this solution does show the transition temperature.

It is generally assumed that the hydration shell of an ion should decrease as the temperature increases as a consequence of the increase in thermal energy which allows the water molecules to escape more easily from the field of the ion. One might expect that as the temperature of the Na_2CO_3 solution increased and passed the hydrate transition temperature that the number of bound molecules of water would decrease and the viscosity of the solution would decrease. However it is observed that the viscosity curve is displaced upwards.



Variation of Viscosity of 1% Na_2CO_3 solution with temperature.
(from reference 1)

This forces the conclusion that the hydration shell of the ion in the lower hydrate state is larger than when the ion is in the higher hydrate state. This effect can be explained by pointing out the possibility that the first layer of water is held by strong hydrate forces and this layer shields the rest of the water from the effect of ionic attraction. When this tightly held water leaves at the transition temperature it is replaced by a larger amount of less strongly held water which is still effective in increasing the apparent diameter of the ion and thus the viscosity increases.

A test of the explanation of the hydrate transition temperatures in dilute solutions would be to add to 0.1F Na_2SO_4 some K_2SO_4, since there is no compound formation between the two salts, and to follow the viscosity of the solution as a function of temperature across the usual hydrate transition temperature. For small concentrations of K_2SO_4 the temperature of the transition should be shifted to a lower value and for larger concentrations, the transition should disappear.

Simpler than making viscosity measurements would be to observe the refractive index of the solutions as refractive index also is affected in the same manner as the viscosity.

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Proposition IV. NSF was reported by Glemser and Haeseler (1) but later Glemser said that he doubted the existence of the compound (2). It is evidently readily converted to NSF_3 as attempts prepare it by direct fluorination of N_4S_4 have been unsuccessful. A synthesis using SF_4 and NH_3 is proposed.

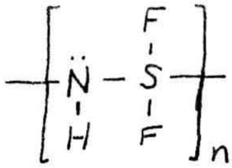
Ammonia reacts with $SOCl_2$ under varying conditions to form several compounds, $HN{=}S{=}O$ (3), $S{=}N\text{-}OH$ (4), and many different polymers of the empirical composition $(NHSO)_n$ (5). It reacts with SOF_2 to form NH_2SOF which is actually a polymer (6). The reaction of NH_3 with SF_4 would as a first step lead to NH_2SF_3 just as NH_2SOCl would be the initial species in the combination of NH_3 and $SOCl_2$. Then setting up parallel reactions

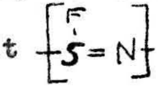
$$\begin{array}{l} NH_2\text{-}SF_3 \rightarrow NH{=}SF_2+HF \\ NH_2SOCl \rightarrow NH{=}SO+HCl \\ \qquad\qquad\qquad \downarrow \\ \qquad\qquad\quad \text{polymers} \end{array}$$

or

$$\begin{array}{l} NH_2SF_3+NH_3 \rightarrow NH_2SF_2NH_2+HF \\ NH_2SOCl+NH_3 \rightarrow NH_2SONH_2+HCl \\ \qquad\qquad\qquad\qquad \Big\downarrow \text{ isomerizes} \\ \qquad\qquad\qquad NH_4^+ \; O=S=N^- \end{array}$$

$HN{=}SF_2$ is the hydrogen analog of the recently prepared organoiminosulfur difluorides $RN{=}SF_2$ (7). These compounds have remarkable thermal stability although they are chemically quite reactive. One can compare the chemical reactivity of thionylimide and the organothionylimides. The latter have been known since 1893 when Michaelis first prepared them (8). CH_3 $N{=}S{=}O$ and $C_6H_5N{=}S{=}O$ are quite stable while $HN{=}S{=}O$ readily polymerizes. Carrying the parallelism further it is possible that $HN{=}SF_2$ would polymerize to



However, there is an alternative reaction that is unavailable to $HN{=}SO$; another HF molecule can be eliminated, yielding NSF. The polymer itself, if it forms, could eliminate HF leaving a polymer with a unit  $\left[\overset{F}{S}{=}N \right]$. The known polymers of NSF are the ring compounds $S_3N_3F_3$ (9) and $N_4S_4F_4$ (10). These polymers however do not depolymerize to NSF on heating. $N_4S_4F_4$ breaks down on heating to form SNF (10).

By a reaction analogous to the reaction between amines and $SOCl_2$, NSF may have been prepared when Hasek, Smith, and Engelhardt treated benzamide with SF_4; the products were benzotrifluoride and, as they assumed, SOF_2 (11). Since the gaseous products of this synthesis were of no interest the gas in the reaction vessel was vented off. There is no report of any solid sulfur-containing products. Stoichiometry requires that the sulfur and nitrogen in the starting materials show up somewhere. Since they found that the first step in the reaction is the formation of the aryl fluoride the initial step of the reaction should be written

$$\phi\, CONH_2 + SF_4 \rightarrow \phi\, COF + SF_3NH_2$$

The SF_3NH_2 should decompose to NSF and HF as described above. The reaction between SF_4 and NH_3 would not be complicated by the fluorination of benzamide.

NSF may be considered as a derivative of SF_4 in the same manner that NSF_3 is considered a derivative of SF_6. SF_4 utilizes a d orbital for bonding as evidenced by the C_{2v} symmetry of the molecule (12). NSF would be using the same orbitals and so would have a bent rather than linear structure. The bond distances should correspond to normal S-F single bond and a normal N-S triple bond. These would predict that the frequencies of the stretching modes should be ~800 cm^{-1} for the S-F stretch and ~1500 cm^{-1} for the N-S stretching mode.

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Proposition V. The complexity of metal-metal bonds investigated has gone from the simple Hg-Hg bond in Hg^{++} to the tantalum octahedron in $Ta_6Cl_{12}^{++}$ (1). The structure of a slightly more complex system, the Pb_9^{-4} ion is proposed and an experimental method using the diffraction of x-rays from solutions of the ion is suggested.

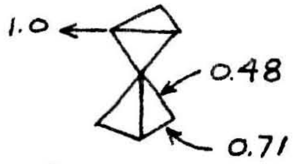
That lead dissolved in solutions of sodium in liquid ammonia was noted by Joannis (2). The equilibrium sodium to lead ratio was not settled until Smyth carefully determined the number of moles of lead deposited on the anode per faraday of current passed (3). He found the now accepted value of 9/4. This remained the only value observed until Zintl carried out potentiometric titrations of sodium in liquid ammonia with solutions of PbI_2 (4). He found inflection points in the potential curve that corresponded to the formation of Pb_7^{-4} as well as Pb_9^{-4}. The Pb_7^{-4} equivalence point was found only in the more dilute solutions. The concentration of Pb_9^{-4} produced during these titrations was small as the limiting factor was the small solubility of PbI_2 in liquid ammonia. Further addition of Pb^{++} to solutions containing Pb_9^{-4} precipitates metallic lead.

The alloy Na_4Pb_9 does not exist in the solid phase (5). On evaporation of solutions in liquid ammonia the solid residue consists of sodium-rich alloys and pyrophoric lead metal (4).

The crystal structure of NaPb has been determined by Marsh and Shoemaker (6). They found that the lead atoms were clustered into almost regular tetrahedra with edges of 3.146 and 3.162A. Calculating the bond numbers from the observed bond distances they found that lead had 2.9 bond orbitals rather than the usual 2.56 and that the sodium has 1.5 orbitals rather than the normal 1. The increased number of orbitals is produced by the transfer of electrons from the hyperelectronic atom, lead, to the hypoelectronic atom, sodium.

Zintl regarded the anions as $Pb(Pb)_6^{-4}$ and $Pb(Pb)_8^{-4}$ with all of the outer lead atoms coordinated to a single central lead. If, as he suggests, the tetragonal prism or antiprism exists in the Pb_9^{-4} ion a considerable shift in the structure would be required when Pb^{++} is added to neutralize the ions and form metallic lead.

I feel that the structures should be based on the known tetraheral units found by Marsh and Shoemaker in NaPb. In Pb_7^{-4} the structure has two tetrahedra with a corner in common. If the lead has 2.9 bonding orbitals the central atom saturates its bonding with 0.48 bond to each of the six other atoms, and the outer six atoms have to have (1/6)x4x1.5 or 1.0 orbital per atom free to satisfy the bonding to sodium. The remaining 1.42 orbitals are shared with the other two Pb atoms in the tetrahedron.



Pb_7^{-4} ion with bond numbers and bonding orbitals

The 0.71 bonds would be 3.09A long and 0.48 bonds would be 3.19A long based on D(1)=3.004 and D(n)=D(1)-0.601 log n (7).

In the Pb_9^{-4} ion there are two possible structures based on a tetrahedral unit.

(a) (b)

Pb_9^{-4} ion with bond numbers

In (a) the atoms forming the center triangle again have 0.48 bonds to each of the outer four Pb's in the adjacent tetrahedra and to the corner atoms of the triangle. Each of the six outer atoms has 1.0 orbital free to satisfy the bonding to sodium. This requires that the bond between the two outer atoms in a tetrahedron be 0.93 bond, of length 3.03A. All the other bonds are 0.48 bond of length 3.19A.

In (b) the outer three atoms each have 1.5 orbitals free and the upper three have 1/3(1.5) orbitals free. All bonds are 0.48 bonds of length 3.19A.

Structure (a) has two symmetrical sites for the entry of two neutralizing Pb^{++} ions but the structure must change upon their entry in order to assume the face-centered cubic structure of metallic lead.

Structure (b) on the other hand has one site at the vacant top of the tetrahedron which would complete a three layer unit of the face-centered structure. The second Pb^{++} could be positioned on any of the centers of the now complete tetrahedron and a small particle of metallic lead would result.

The difference between the $Pb(Pb)_8^{-4}$ structure and the tetrahedral structure of the Pb_9^{-4} ion may be determined by x-ray diffraction as other complexes in solution have been done (8, 9). The requirement for the possibility is that the solvent scattering power be significantly smaller than that of the compound under investigation. The total scattering power of the solute depends on the concentration of the solute and in a rough approximation, the number of electrons in a molecule of the solute.

Although the saturation concentration of sodium in liquid ammonia at -33°C is ~15M moles/liter let us take as a practical example a reported case of dissolving lead in 0.3M sodium in liquid ammonia (3). If the scattering from the Pb atoms is assumed to be independent, the scattering of the NH_3 molecules and the Na^+ ions is less than half of the scattering from the lead.

Two conditions have been assumed that are unfavorable. The concentration of lead may be increased and the lead atoms are not scattering independently but would show interference effects since they are bound together in the ions.

Zintl's proposed structure of eight leads coordinated to a central lead atom cannot be a body centered cube as the central atom does not have sufficient orbitals to form bonds of the strength required to make the distance equal to half of the body diagonal of a cube. The bonds from the central to the outer atoms are .36 bonds of length 3.27A; the bonds between adjacent outer atoms are .90 bonds of length 3.03A. The body diagonal of a cube with edge 3.03A is 5.25A while twice the central atom-outer atom bond length is 6.54A. Accordingly the structure will be in the most symmetrical cases, a tetragonal prism or antiprism with the ninth lead at its center.

The schematic radial distribution functions for the tetrahedral structures (a) and (b) and the tetragonal prism and antiprism are shown in figure P1. The difference is sufficient so that the experimental scattering curves will be quite different for the tetrahedral structures and the tetragonal structures.

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Figure P1. Radial distribution functions of tentative structures.

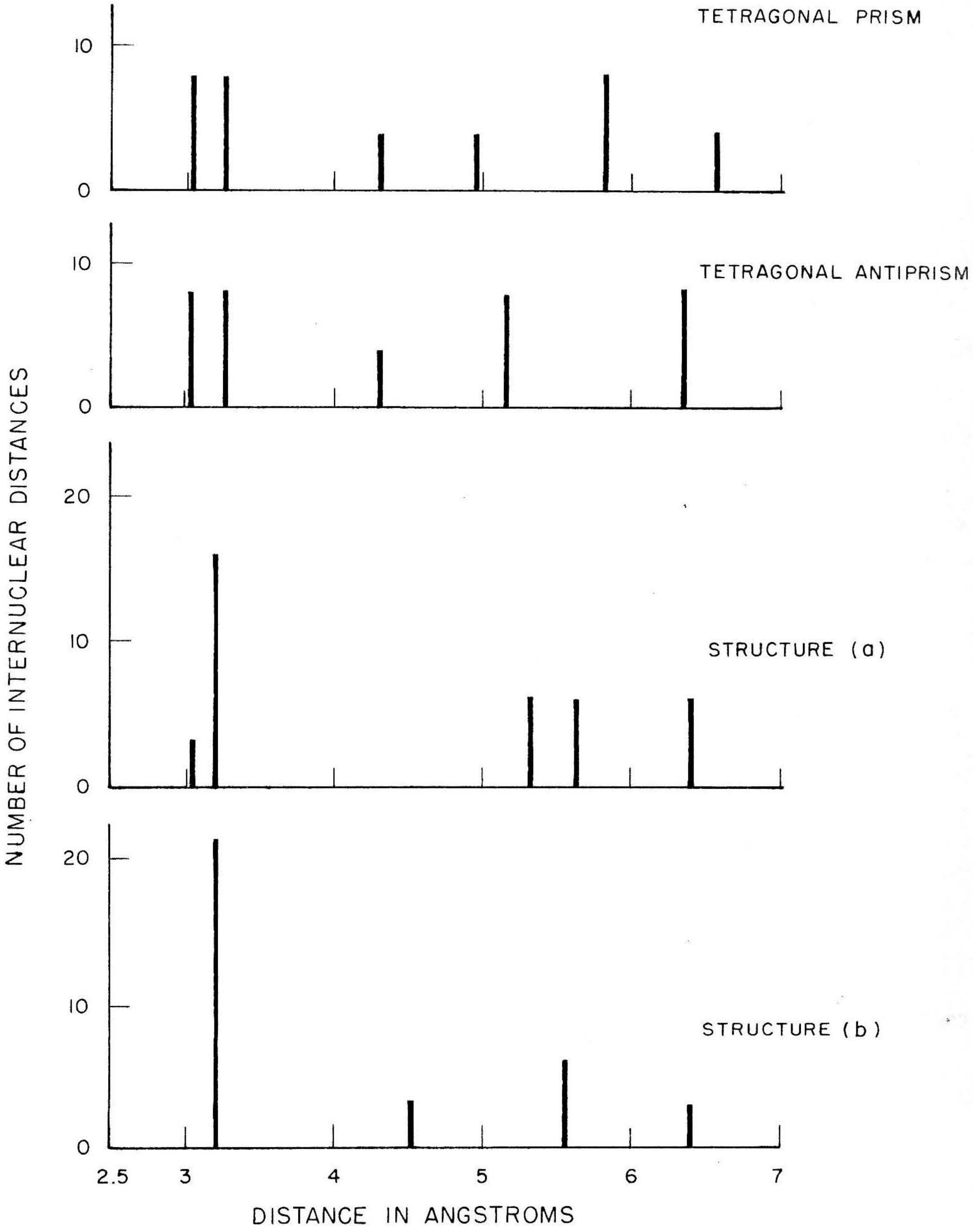
TETRAGONAL PRISM
TETRAGONAL ANTIPRISM
STRUCTURE (a)
STRUCTURE (b)
NUMBER OF INTERNUCLEAR DISTANCES
DISTANCE IN ANGSTROMS
0
10
20
2.5
3
4
5
6
7

FIG. P1

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